PB89-220537

Proceedings: 1989 Joint Symposium on Stationary Combustion NOx Control. Held in San Francisco, California on March 6-9, 1989. Volume 2

Electric Power Research Inst., Palo Alto, CA

Prepared for:

Environmental Protection Agency, Research Triangle Park, NC

Jun 89

U.S. Department of Commerce
National Technical Information Service
NTIS

PB89-220537

EPA-600/9-89-062b
June 1989

PROCEEDINGS:

1989 JOINT SYMPOSIUM ON STATIONARY COMBUSTION NO_x CONTROL

San Francisco, CA, March 6-9, 1989
Volume 2

Compiled by

Claudia Runge
Electric Power Research Institute
3412 Hillview Avenue
Palo Alto, CA 93404

EPA Project Officer:
William P. Linak

U.S. Environmental Protection Agency
Air and Energy Engineering Research Laboratory
Research Triangle Park, NC 27711

EPRI Project Manager:
David Eskinazi

Electric Power Research Institute
3412 Hillview Avenue
Palo Alto, CA 93404

AIR AND ENERGY ENGINEERING RESEARCH LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
U.S. ENVIRONMENTAL PROTECTION AGENCY
RESEARCH TRIANGLE PARK, NC 27711

REPRODUCED BY
U.S. DEPARTMENT OF COMMERCE
NATIONAL TECHNICAL INFORMATION SERVICE
SPRINGFIELD, VA. 22161

TECHNICAL REPORT DATA
(Please read Instructions on the reverse before completing)

1. REPORT NO.
EPA/600/9-89/062b

2.

3. RECIPIENT'S ACCESSION NO.
PB89 220537/AS

4. TITLE AND SUBTITLE
Proceedings: 1989 Joint Symposium on Stationary Combustion NOx Control, San Francisco, CA, March 6-9, 1989, Volume 2

5. REPORT DATE
June 1989

6. PERFORMING ORGANIZATION CODE

7. AUTHOR(S)
Claudia Runge, Compiler

8. PERFORMING ORGANIZATION REPORT NO.

9. PERFORMING ORGANIZATION NAME AND ADDRESS
Electric Power Research Institute
3412 Hillview Avenue
Palo Alto, California 93404

10. PROGRAM ELEMENT NO.

11. CONTRACT/GRANT NO.
NA (Inhouse)

12. SPONSORING AGENCY NAME AND ADDRESS
EPA, Office of Research and Development
Air and Energy Engineering Research Laboratory
Research Triangle Park, NC 27711

13. TYPE OF REPORT AND PERIOD COVERED
Proceedings; 3/87-3/89

14. SPONSORING AGENCY CODE
EPA/600/13

15. SUPPLEMENTARY NOTES AEERL project officer is William P. Linak, Mail Drop 65, 919/541-5792.

16. ABSTRACT
The proceedings document presentations at the 1989 Joint Symposium on Stationary Combustion NOx Control, held March 6-9, 1989, in San Francisco, CA. The symposium, sponsored by the U.S. EPA and EPRI, was the fifth in a series devoted solely to the discussion of control of NOx emissions from stationary sources. Topics discussed included low-NOx combustion developments such as burner design modifications and reburning; coal-, oil-, and gas-fired boiler applications; flue gas treatment processes; fundamental combustion studies; and industrial and commercial applications. Also presented were manufacturers' updates of commercially available technology and an overview of environmental issues involving NOx control. The 4-day meeting was attended by persons from 14 nations. More than 50 papers were presented by EPA and EPRI staff members, utility company representatives, boiler and related equipment manufacturers, research and development groups, and university representatives. The proceedings are in two volumes. Volume 1 includes background, combustion NOx developments I and II, manufacturer's update, advanced combustion technology, and incineration. Volume 2 includes SCR coal applications, fundamental combustion research, post combustion NOx control development, fundamental combustion research, new developments, and oil and gas combustion.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS		b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group	
Pollution	Toxicity	Pollution Control	13B	06T
Nitrogen Oxides	Measurement	Stationary Sources	07B	
Combustion	Electric Power Plants	Hazardous Waste	21B	10B
Fossil Fuels	Boilers	Municipal Waste	21D	13A
Catalysis Incinerators	Research Development	Research and Development	07D	14F
Wastes			14G	

18. DISTRIBUTION STATEMENT
Release to Public

19. SECURITY CLASS *(This Report)*
Unclassified

20. SECURITY CLASS *(This page)*
Unclassified

21. NO. OF PAGES
544

22. PRICE

EPA Form 2220-1 (9-73)

ABSTRACT

The 1989 Joint Symposium on Stationary Combustion NO_x Control was held in San Francisco, California, March 6-9, 1989. This Symposium, jointly sponsored by EPRI and EPA, had as its objective the exchange of information regarding recent technological and regulatory developments pertaining to stationary combustion NO_x control in the United States and abroad. Topics covered during the Symposium included: low-NO_x combustion development; coal-, oil-, and gas-fired boiler applications; flue gas treatment; fundamental combustion studies; and environmental and regulatory issues. The Symposium Proceedings is published in two volumes.

DISCLAIMER

The work described in the papers in this volume was not funded by the U.S. Environmental Protection Agency. The contents do not necessarily reflect the views of the Agency and no official endorsement should be inferred.

PREFACE

The 1989 Joint Symposium on Stationary Combustion NO_x Control was held March 6-9, 1989, in San Francisco, California. This symposium, jointly sponsored by EPRI and EPA, was the fifth of its kind devoted solely to the discussion of control of NO_x emissions from stationary sources. Specific topics discussed included the low-NO_x combustion developments such as burner design modifications and reburning, coal-, oil-, and gas-fired boilers applications, flue gas treatment processes, fundamental combustion studies, and industrial and commercial applications. Also presented were manufacturers' updates of commercially available technology and an overview of environmental issues involving NO_x control.

The four-day meeting was attended by persons from 14 nations. Over fifty papers were presented by EPRI and EPA staff members, utility company representatives, boiler and related equipment manufacturers, research and development groups, and university representatives.

Symposium cochairpersons were David Eskinazi, Project Manager in the Air Quality Control Program of EPRI's Generation and Storage Division; and Dr. William P. Linak, Chemical Engineer in the Combustion Research Branch of the EPA's Air and Energy Engineering Research Laboratory. Each of the cochairpersons made brief introductory remarks. Mr. David Finnigan, Counsel for the House Energy and Commerce Committee delivered the keynote address. Written manuscripts were not prepared for the introductory remarks or keynote address; therefore, they are not published herein.

The Proceedings of the 1989 Joint Symposium have been compiled in two volumes. Volume 1 contains papers from the following sessions:

- Session 1: Background
- Session 2: Combustion NO_x Developments I
- Session 3: Combustion NO_x Development II
- Session 4: Manufacturer's Update
- Session 5A: Advanced Combustion Technology
- Session 5B: Incineration

Papers from the following sessions are contained in Volume 2:

- Session 6A: SCR Coal Applications
- Session 6B: Fundamental Combustion Research
- Session 7A: Post Combustion NO_x Control Development
- Session 7B: Fundamental Combustion Research
- Session 8: New Developments
- Session 9: Oil and Gas Combustion Applications

Also included in both volumes is an Appendix listing the Symposium attendees.

Papers from the following sessions are contained in Volume 2:

- Session 6A: SCR Coal Applications
- Session 6B: Fundamental Combustion Research
- Session 7A: Post Combustion NO_x Control Development
- Session 7B: Fundamental Combustion Research
- Session 8: New Developments
- Session 9: Oil and Gas Combustion Applications

Also included in both volumes is an Appendix listing the Symposium attendees.

CONTENTS

VOLUME 1

Paper Page

SESSION 1: BACKGROUND
Chairman: I. Torrens, EPRI

"Innovative Clean Coal Technology NO_x Control Technology,"J. Temchin and H. Feibus 1-1

"Policies for NO_x Control in Europe," A.-K. Hjalmarsson and J. Vernon 1-9

"Environmental Effects of Nitrogen Oxides," R. Perhac 1-29

"N_2O Emissions from Fossil Fuel Combustion," W. Linak, J. McSorley, R. Hall, J. Ryan, R. Srivastava, J. Wendt, and J. Mereb 1-37

"Measurement of N_2O from Combustion Sources," L. Muzio, M. Teague T. Montgomery, G. Samuelsen, J. Kramlich, and R. Lyon 1-55

SESSION 2: COMBUSTION NO_x DEVELOPMENTS I
Chairman: D. Eskinazi, EPRI

"The Application of Combustion Modifications for NO_x-Reduction to Low-Rank Coal-Fired Boilers," K. Hein 2-1

"Predicting Boiler and Emissions Performance by Comparative Turbulent/Low NO_x Burner Testing on a Large Test Facility," J. Vatsky and C. Allen 2-23

"Reduction of NO_x Emissions from a 500MW Front Wall Fired Boiler," P. Beard, W. Brooks, K. Johnson, K. Matthews, P. Wells, and J. Vatsky 2-53

"NO_x Emissions Results for a Low-NO_x PM Burner Retrofit," R. Thompson, G. Shiomoto, D. Shore, M. McDannel, and D. Eskinazi 2-67

"Retrofit and Boiler Performance Evaluation of the Low NO_x PM Firing System at Kansas Power & Light," R. Lewis, A. Kwasnik, R. LaFlesh, and D. Eskinazi 2-87

"ENEL's Ongoing and Planned NO_x Control Activities," A. Benanti,D. Bonolis, R. Tarli, A. Baldacci, A. Piantanida, and A. Zennaro 2-109

Paper Page

SESSION 3: COMBUSTION NO_x DEVELOPMENT II
Chairman: R. Hall, EPA

"Pilot Evaluation of Reburning for Cyclone Boiler NO_x Control," H. Farzan, L. Rodgers, G. Maringo, A. Kokkinos, and J. Pratapas 3-1

"Application of Reburning to a Cyclone Fired Boiler," R. Borio, A. Kwasnik, D. Anderson, D. Kirchgessner, R. Lott, A. Kokkinos, and S. Durrani 3-27

"Design Methods for Low-NO_x Retrofits of Pulverized Coal-Fired Utility Boilers," S. Morita, K. Kiyama, T. Jimbo, K. Hodozuka, and K. Mine 3-53

"New Approach to NO_x Control Optimization of NO_x and Unburnt Carbon Losses," M. Kinoshita, T. Kawamura, S. Kaneko, and M. Sakai 3-73

"The XCL Burner - Latest Developments and Operating Experience," A. LaRue 3-93

"Application of Low NO_x Combustion Technologies to a Low Volatile Coal Firing Boiler," S. Miyamae, T. Kiga, and K. Makino, and K. Suzuki 3-111

SESSION 4: MANUFACTURER'S UPDATE
Chairman: G. Offen, EPRI

"NO_x Control: The Foster Wheeler Approach," J. Vatsky 4-1

"NO_x Control Update - 1989," A. LaRue, and P. Cioffi 4-17

"1989 Update on NO_x Emission Control Technologies at Combustion Engineering," R. Donais, M. Cohen, and M. McCartney 4-37

"Status of NO_x Control Technology at Riley Stoker," R. Lisauskas, E. Reicker, and T. Davis 4-57

SESSION 5A: ADVANCED COMBUSTION TECHNOLOGY
Chairman: N. Holt, EPRI

"The Conversion of Fuel-Nitrogen to NO_x in Circulating Fluidized Bed Combustion," Y. Lee, and M. Hiltunen 5A-1

"NO_x Control in Coal Gasification Combined Cycle (IGCC) Systems," N. Holt, E. Clark, and A. Cohn 5A-17

Paper Page

"Development of NO_x Control Technologies for Coal-Fueled Stationary Diesel Power Plants," S. Johnson, C. Senior, C. Katz, and R. Wilson, Jr. 5A-29

SESSION 5B: INCINERATION
Chairman: W. Linak, EPA

"Reduction of NO_x Emissions from MSW Combustion Using Gas Reburning," C. Penterson, D. Itse, H. Abbasi, Y. Wakamura, and D. Linz 5B-1

"Application of Low NO_x Precombustor Technology to the Incineration of Nitrogenated Wastes," R. Srivastava, J. Ryan, W. Linak, R. Hall, J. McSorley, and J. Mulholland 5B-23

"The Effect of Fuel Nitrogen on NO_x Emissions from a Rotary-Kiln Incinerator," J. Lighty, D. Gordon, D. Pershing, W. Owens, V. Cundy, and C. Leger 5B-45

VOLUME 2

SESSION 6A: SCR COAL APPLICATIONS
Chairman: E. Cichanowicz, EPRI

"Reduction of Nitrogen Oxides from Coal-Fired Power Plants by Using the SCR Process. Experiences in the Federal Republic of Germany with Pilot and Commercial Scale Denox Plants," B. Schönbucher 6A-1

"Experience Gained by Neckarwerke from Operation of SCR $DeNO_x$ Units," P. Necker 6A-19

"Recent Developments in the SCR System and Its Operational Experiences," H. Kuroda, I. Morita, T. Murataka, F. Nakajima, Y. Kato, and A. Kato 6A-39

"The First De-NO_x Installation in the Netherlands, a Demonstration Project at EPON - Nijmegen Power Station," J. Koppius-Odink, W. Weier, and W. Prins 6A-57

"Operating Experience of SCR Systems at EPDC's Coal-Fired Power Station," T. Mori, and N. Shimizu 6A-85

Paper Page

"Technical Feasibility and Economics of SCR NO_x Control in Utility Applications," C. Robie, P. Ireland, and J. Cichanowicz 6A-105

SESSION 6B: FUNDAMENTAL COMBUSTION RESEARCH
Chairman: B. Martin, EPA

"Prediction of Fuel and Thermal NO in Advanced Combustion Systems," R. Boardman, and L. Smoot 6B-1

"NO_x Reduction in Fuel-Rich Natural Gas and Methanol Turbulent Diffusion Flames," M. Toqan, J. Teare, J. Beer, A. Weir, Jr., and L. Radak 6B-21

"Reduction of Fuel-NO by Increased Operating Pressure in a Laboratory-Scale Coal Gasifier," K. Nichols, P. Hedman, and A. Blackham 6B-39

"Evolution and Reaction of Fuel Nitrogen During Rapid Coal Pyrolysis and Combustion," G. Haussmann, and C. Kruger 6B-61

"The Effect of Process Variables on NO_x and Nitrogen Species Reduction in Coal Fuel Staging," K. Knill, and M. Morgan 6B-75

"NO_x Emissions in a Pilot Scale Circulating Fluidized Bed Combustor," J. Zhao, J. Grace, C. Lim, C. Brereton, R. Legros, and E. Anthony 6B-93

SESSION 7A: POST COMBUSTION NO_x CONTROL DEVELOPMENT
Chairman: C. Sedman, EPA

"Design and Operation of the SCR-Type NO_x-Reduction Plants at the Dürnrohr Power Station in Austria," M. Novak, and H. Rych 7A-1

"Denox Catalytic Converters for Various Types of Furnaces and Fuels - Development, Testing, Operation," L. Balling, and D. Hein 7A-27

"Assessment of Japanese SCR Technology for Oil-Fired Boilers and Its Applicability in the U.S.A.," P. Lowe, W. Ellison, and L. Radak 7A-41

"NO_x Control in a Brown Coal-Fired Utilty Boiler," J. Hoffmann, J. von Bergmann, D. Bökenbrink, and K. Hein 7A-53

SESSION 7B: FUNDAMENTAL COMBUSTION RESEARCH
Chairman: W. Linak, EPA

"Formation of Nitrous Oxide from NO and SO_2 During Solid Fuel Combustion," G. deSoete 7B-1

Paper Page

"Fuel Nitrogen Mechanisms Governing NO_x Abatement for Low and High Bank Coals," J. Wendt, A. Bose, and K. Hein 7B-14

"Methanol Injection - A New Method for No_x and SO_3 Control," R. Lyon 7B-29

SESSION 8: NEW DEVELOPMENTS
Chairman: E. Plyler, EPA

"Catalyst Poisoning in the Selective Catalytic Reduction Reaction," R. Yang, J. Chen, M. Buzanowski, and J. Cichanowicz 8-1

"Catalytic Filter Bags," M. Kalinowski, and P. Aubourg 8-9

"Advanced In-Furnace NO_x Control in New European Coal-Fired Power Plant," K. Bendixen, and J. Pedersen 8-15

"Two-Stage DeNO_x Process Test Data from Switzerland's Largest Incineration Plant," D. Jones, L. Muzio, E. Stocker, P. Nüesch, S. Negrea, G. Lautenschlager, E. Wachter, and G. Rose 8-21

"Effects of Catalyst Developments of the Economics of Selective Catalytic Reduction," T. Gouker, J. Solar, and C. Brundrett 8-27

"Full Scale Demonstration of Additive NO_2 Reduction(1) with Dry Sodium Desulfurization," V. Bland 8-33

"Shell Process for Low-Temperature NO_x Control," F. Goudriaan, C. Mesters, and R. Samson 8-39

"NO_x Reduction of Waste Incineration Flue Gas," B. Herrlander 8-45

"Reburning and Repowering for NO_x Control on Large Utility Boilers," S. Chen, E. Moller, D. Pershing, and A. Walters 8-51

SESSION 9: OIL AND GAS COMBUSTION APPLICATIONS
Chairman: A. Kokkinos, EPRI

"Retrofit of an Advanced Low-NO_x Combustion System at Hawaiian Electric's Oil-Fired Kahe Generating Station," J. Yee, R. Freitas, D. Giovanni, S. Kerho, and M. McElroy 9-1

"Gas Turbine Nitrogen Oxide (NO_x) Control Current Technologies and Operating Experiences," L. Angello, and P. Lowe 9-19

"Demonstration of an Automated Urea Injection System at Encina Unit 2," J. Nylander, M. Mansour, and D. Brown 9-35

Paper Page

"Retrofit Implications of a Low NO_x Burner System on a 230-MW Oil- and Gas-Fired Boiler," J. Carnevale, and J. Klueger 9-57

"Retrofitting Low-NO_x Burners for Gas and Oil Firing," J. Gerdes, Jr., R. Waibel, and L. Radak 9-75

"Engineering Evaluation of Combined NO_x/SO_2 Removal Processes: Interim Report," W. DePriest, J. Jarvis, and J. Cichanowicz 9-89

APPENDIX A: LIST OF ATTENDEES

Session 6A

SCR COAL APPLICATIONS

Chairman: E. Cichanowicz, EPRI

REDUCTION OF NITROGEN OXIDES FROM COAL-FIRED POWER PLANTS BY USING THE SCR PROCESS. EXPERIENCES IN THE FEDERAL REPUBLIC OF GERMANY WITH PILOT AND COMMERCIAL SCALE DENOX PLANTS

Dr. B. Schönbucher
Energie-Versorgung Schwaben AG
P.O. Box 10 12 43
7000 Stuttgart 10
Federal Republic of Germany

ABSTRACT

According to legal requirements in the Federal Republic of Germany (FRG) the NO_x concentration of flue gas from coal-fired power plants has to be reduced to < 200 mg/m^3 (s.t.p., dry) until 1990 latest. Hard coal-fired power plants with an electric capacity of a total of about 28 200 MW are retrofitted with DENOX plants mainly using the selective catalytic reduction process (SCR process). In hard coal-fired power plants with a dry bottom boiler the DENOX plants are mainly operating as high dust systems. Power plants with wet bottom boiler have the DENOX plant appended to the flue gas desulphurisation plant (FGD plant) as a tail end system. The decision for these two SCR arrangements based on several years of experiences with pilot plants. The essential knowledge out of the operation of the pilot plants and experiences with commercial scale DENOX plants in the FRG will be presented.

1. INTRODUCTION

New NO_x emission standards for flue gas from power stations have been established in the FRG in April 1984. According to the legal requirements the NO_x concentration of flue gas from coal-fired power plants have to be reduced to below 200 mg/m^3 (s.t.p., dry) until 1990 latest. Hereof affected are coal-fired power plants with an electric capacity of a total of 37 500 MW.

In power plants with an electric capacity of 9 300 MW domestic lignite is fired. For these power plants primary measures such as off-stoichiometric combustion (biased burner firing, burner out of service and overfire air) and flue gas recirculation in combination with low excess air firing will be used to reduce the NO_x concentration below 200 mg/m^3 (s.t.p., dry). For some of the lignite-fired power plants the application of the selective non-catalytic reduction (SNCR) process is planned as an additional measure/1,2/.

For hard coal-fired power plants with an electric capacity of a total of 28 200 MW mainly the so called selective-catalytic reduction process is applied. The SCR process was developed in Japan and used there on a commercial basis for the first time. In order to test this process under conditions of the German power plants more than 70 pilot plants have been operated during the last 4 years. Since December 1985 the first commercial scale DENOX plant according to the SCR process for a hard coal-fired power plant is in operation. At present 28 hard coal-fired power plants with an electric capacity of more than 6 400 MW are retrofitted with a DENOX plant using the SCR process.

The first part of this report shows the essential results from the pilot plant. The second part will report on experiences with commercial scale plants for hard coal-fired power plants in the FRG.

2. HARD COAL-FIRED POWER PLANTS IN THE FRG

In the FRG hard coal-fired power plants are mainly operated in the middle load range with 3 000 to 5 000 hours of operation per year. Daily start-up and shutdown as well as week end shutdown between April and September are the usual operating conditions. At present 90 million tons per year hard coal are used for the generation of current of which 85 % are domestic hard coal. Table 1 shows essential datas of German hard coal.

Table 2 shows the flue gas data at the exit of the economizer. The NO_x concentration depends on the layout of the boilerroom, the quality of coal, the temperature of air for combustion and the excess air as well as on the type of firing (wet or dry firing) and on primary measures for the NO_x reduction. About half of the hard coal-fired power plants is equipped with wet bottom boilers while the other half has dry bottom boilers.

Complementary in Table 3 the essential compounds of fly ash out of hard coal-fired power plants are summarized.

Since the middle of the 70ties the FRG started with considerable efforts to reduce the NO_x concentration by optimizing firing conditions (e.g. using low NO_x burners and over fire air ports). Normally, the NO_x concentration of flue gas can be reduced to between 650 mg/m^3 and 800 mg/m^3 for dry bottom boilers by using primary measures. For wet bottom boilers the NO_x concentration mainly is between 1 300 and 2 000 mg/m^3 (s.t.p., dry).

This means that the NO_x emission standard of 200 mg/m^3 (s.t.p., dry) in hard coal-fired power plants can not be met with primary measures only. The application of secondary NO_x reduction measures is necessary.

3. SCR PROCESS

In the FRG most pilot- and commercial scale plants for NO_x reduction are based on the selective catalytic reduction process (SCR process) developed in Japan (Figure 1). With the SCR process, a catalyst is used to reduce the flue gas components NO and NO_2 selectively to nitrogen and water by adding ammonia (NH_3). The catalysts differ in their chemical composition and their shape.

The honeycomb and metal carrier plate catalysts consist of surface active titanium dioxide (TiO_2) as carrier material. Vanadium pentoxide (V_2O_5) and tungsten trioxide (WO_3) are the most important active components /3/. Also suitable for the NO_x reduction is activated carbon /4/. The optimal operating temperature for catalysts on basis TiO_2 is between 280 °C and 400 °C. Activated carbon is preferred for temperatures of around 100 °C.

In the FRG the SCR process was tested in various configurations (Figure 2):

- upstream the air preheater ("high dust system")
- between the electrostatic precipitator and the flue gas desulphurization plant (FGD plant)
- downstream the FGD plant ("tail end system").

In the FRG most FGD systems for power plants work on the wet-scrubber process using lime or limestone as absorbent and high purity gypsum as byproduct. In some power plants the spray-dryer process is used for SO_2 reduction.

4. RESULTS FROM DENOX PILOT PLANTS USING THE SCR PROCESS

4.1. DENOX pilot plants in the FRG

The most DENOX pilot plants used the SCR process /5/. In the majority of cases the SCR process was tested as a

- high dust system for
  - -- hard coal-fired power plants with dry or wet bottom boilers

-- lignite-fired power plants and as a

- tail end system for hard coal-fired plants with wet bottom boilers.

4.2. Catalyst properties

The main object of tests in the pilot plants was to determine the properties of catalyst. These inculde (Table 4):

- The NO_x removal efficiency (η_{NO_x})

  The NO_x removal efficiency is influenced by a number of parameters like:

  -- the NO_x concentration at inlet into reactor and exit from reactor ($C^{in}_{NO_x}$, $C^{ex}_{NO_x}$),

  -- the flue gas temperature (T_{FG}),

  -- the molar ratio NH_3/NO_x (X),

  -- the catalyst capacity. This is normally defined as area velocity (AV: quotient of flue gas volume stream V_{FG} $[m^3/h]$ and catalyst surface A_{cat} $[m^2]$),

  -- oxygen concentration C_{O_2} and

  -- chemical and physical data of the catalyst.

- The catalyst activity (k_t)

  Corresponding to the Eley Rideal mechanism NH_3 is chemically absorbed in a fast running reaction step and reacts with NO from the gas phase. This reaction can be considered as an apparent first order reaction /6/. The various catalysts which differ with respect to structure and composition can be characterized by this k value. With the first admission of flue gas a desactivation of the catalyst begins. The decrease of activity mainly is influenced by the flue gas and ash composition.

- The NH_3-slip

  In order to keep the NO_x removal efficiency at a constant level during catalyst life-time, the NH_3 volume flow must be increased from time to time. By this way loss of catalyst activity can be compensated. However, the NH_3 concentration in the flue gas downstream the DENOX plant thereby rises (NH_3 slip). As a result of unavoidable secondary reactions of ammonia with other flue gas components such as SO_3 or HCl the formation of ammonia salts increases. On the basis of operating results obtained from Japan the admissible NH_3 slip was limited to below 5 vppm (= 3.8 mg/m^3) by the installation suppliers in order to limit negative effects in the plant equipment downstream the DENOX plant such as air preheater or FGD plant. An other point is to avoid an unallowable contamination of the fly ash with NH_3 /7-10/.

- The SO_2 conversion rate

  Finally the SO_2 conversion rate is another important charcteristic of the catalyst. It must be considered together with the NH_3 slip.

The investigations in pilot plants have shown that with a NH_3/NO_x molar ratio higher than 0.85 to 0.95 a measurable NH_3 slip will occur within a relatively short operating period. If the molar ratio and thus the NO_x removal efficiency is raised even further there will be a greater risk that the specified limit for the NH_3 slip will soon be reached or exceeded.

It is therefore important to determine how long the NO_x removal efficiency can be maintained on a certain level without exceeding the NH_3 slip limit of 5 vppm. The results for the progress of activity with various types of firing, fuels and configurations are shown in Figure 3 /11/. K_0 is the activity coefficient of fresh catalyst and k_t after an operation period of t. Characteristic is that the decrease of the activity in relationship to the operating time is relativly small for high dust SCR systems downstream hard coal-fired boilers with dry firing and for tail end SCR systems. These results are in good correlation with japanese results for hard coal-fired power plants.

In case of the high dust SCR system downstream hard coal-fired boilers with wet firing and 100 % ash recirculation the activity decline runs very steep /11,12/. Investigations in the FRG indicate that this decline mainly is caused by gaseous arsenic compounds in the flue gas /13,14/. Besides the arsenic content of the coal (with domestic coal mostly < 5 vppm, partly up to 20 - 25 vppm) the type of firing and the CaO content of the fly ash are of great influence on the arsenic concentration in flue gas.

The high temperatures in the combustion chambers of slag tap furnaces lead to a increased volatilization of arsenic compounds compared to dry bottom firing systems. Experiences showed that for wet bottom boilers with 100 % ash recirculation the concentration of arsenic compounds in the flue gas (upstream air preheater) can reach values up to 1 mg/m^3. The arsenic concentration in the flue gas also depends on the CaO content in fly ash. Arsenicoxid reacts with CaO at temperatures above 500 °C to form calciumarsenit ($Ca_3(AsO_4)_2$):

$$3\ CaO + AsO_3 + O_2 \longrightarrow Ca_3(AsO_4)_2$$

By using the tail end SCR system especially for hard coal-fired boilers with wet bottom firing the catalyst is neither subjected to the full dust content of flue gas nor with components like calcium-, magnesium-, potassiume-, sodium- or arsenicoxid. Experiences have shown that with the tail end system it is possible to use catalysts with considerably higher specific geometric surfaces than in the case of the high dust system (Figure 4). The main reason for this is that the dust concentration of the flue gas downstream the FGD plant normally is below 50 mg/m^3 (s.t.p., dry) so that pitch of the catalyst can be reduced. With the high dust system the pitch is between 7.4 and 7.0 mm. With the tail end system a pitch of 4.2 mm normally is the optimum compromise between specific geometric surface and pressure loss /15,16/.

Moreover by modifying the composition of the catalyst material and/or the manufacturing process, activity can be increased. Compared to high dust systems the comparable catalyst volume with low dust systems can be 50 to 60 % less. At the same time the reaction temperature can be lowerd to about 300 °C. Guaranteed life-time for catalysts is the case of the tail end system is 24000 hours of operation and 5 years in maximum. Guaranteed catalyst life-time for high dust systems downstream boilers with slag-tap firing and 100 % ash recirculation is not more than 12000 hours or 2 years in maximum.

The disadvantages of tail end systems are a markedly higher pressure loss, an expensive reheating system and the cost of fuel needed to cover the temperature loss in the gas preheater /17/.

5. RESULTS FROM COMMERCIAL SCALE DENOX PLANTS USING THE SCR PROCESS

At present 28 hard coal-fired power plants with an electric capacity of a total of 7 470 MW are equipped with DENOX plants using the SCR process. All 28 DENOX plants have been retrofitted. 18 DENOX plants (6 300 MW) were retrofitted as a high dust configuration. Some of these DENOX plants have been in operation since 3 years /11,14,18-26/. 11 DENOX plants (1 070 MW) are erected as tail end systems downstream of the FGD plant. Only two of the power plants with wet bottom boilers are retrofitted with a high dust SCR system.

The first DENOX plant as a tail end SCR system is in operation since September 1987 /27/. DENOX plants for dry bottom boilers are designed for a NO_x reduction efficiency of 75 to 80 %. With a space velocity (SV) of 2 650 to 3 000 [1/h] (nominal pitch: 7.0 - 7.4) guaranteed catalyst life-time is between 12 000 and 16 000 operating hours and a maximum of 3 to 4 years (with a NH_3 slip of < 5 vppm at the end of the warrenty period). The DENOX plants for the two power plants with a wet bottom boiler are designed for a NO_x reduction efficiency of 90 %. The SV in these cases is in the range of 2 000 [1/h]. The expected life-time of the catalysts for these both DENOX plants is about 12 000 operating hours. In both plants a 100 % ash recirculation is not realized and therefore, the arsenic problem should not be so considerable.

The operation of the DENOX plants so far has shown that the expected high NO_x reduction efficiency will be reached. The experiences also show that espescially in case of high dust configurations the flow to the first catalyst layer is of great importance.

The catalyst can only then be used at an optimum when a uniform velocity, temperature and NH_3/NO_x distribution exists upstream from the first catalyst layer and no dust stratification occurs, which locally leads to erosion or plugging of the catalyst. This aim is often very difficult to achieve particularly with retrofits. The best way is to carry out flow tests on scale models in order to receive conclusions for large scale plants. By installation of a flow rectifier layer (dummy) upstream from the first catalyst layer, an optimum design of the reactor hood contour and the positioning of guide plates (baffles) a good velocity distribution with a deviation of 10 - 12 % from the average value can be achieved. Because of the expected unequal distribution of the NO_x and flue gas quantities upstream from the ammonia injection position an injection grid with many individual nozzles (30 - 40 nozzles per square metre) is necessary.

The example of the DENOX plant for Unit 7 of our Heilbronn power station shows some characteristic operation results. Unit 7 has an electric output of 700 MW. It is fired with domestic hard coal and is equipped with a dry bottom boiler and a tangential firing system. The unit is in operation since 1985 with approx. 4 000 operating hours per year. The DENOX plant was retrofitted and is in operation since September 1986. Figure 5 shows essential design data of the DENOX plant /18/.

The NH_3 slip did not increase after 8 500 operating hours. This also applies for the SO_2/SO_3 conversion rate. Above the first catalyst layer soot blowers are installed which are in operation every two weeks. So far the pressure loss increase is lower than expected.

The NO_x concentration at the exit of the DENOX plant works this way that at constant boiler load the value is about 160 - 170 mg/m^3 (s.t.p., dry). In case of load changes the control system ensures that the NO_x limiting value does not exceed 200 mg/m^3 (s.t.p., dry).

In Figure 6 the NO_x decline across the three catalyst layers is shown. This figure gives an example how the main conversion zone for NO_x is at first clearly in the first catalyst layer. The third layer apparently only serves the adjustment of the NH_3 slip. This tendancy remains principally with used catalysts, however, the NO_x conversion shifts increasingly into the second and third layer.

Even though few DENOX plants have more than 10 000 - 12 000 operating hours, it can be assumed that the guaranteed catalyst life-time will be reached. The SCR process as high dust system proves to be a reliable technology for reduction of NO_x concentration to < 200 mg/m^3 (s.t.p., dry) for dry bottom boilers.

Furthermore, the experiences show that erosion or plugging of the catalyst is not to be expected as long as the ash content of the flue gas is below 10 to 12 g/m^3. But the use of soot blowers is necessary. In case of hard coal with relative high ash content erosion and plugging is possible. Because of this it was necessary to exchange the catalyst earlier in some plants.

At present the NH_3 slip normally is determined on wet-chemical methods. Continuously operating measurement instruments are under going tests /23,28/.

The experiences show that with a NH_3 slip of more than 2 vppm fly ash cannot used by the cement industry anymore. This especially applies for hard coal with low ash content (< 5 - 8 %) /29/.

Till now the operation of tail end SCR DENOX plants is without problems. The activity loss of the catalyst is very low as this was already found out in the pilot plants.

At present more than 50 DENOX plants for hard coal-fired power plants with wet bottom boilers and an electric capacity of a total of more than 5 300 MW as the tail end configuration are in operation or under erection.

Essential reasons therefor are the short life-time for catalysts in the high dust system downstream wet bottom boilers and space problems when placing a DENOX plant upstream of the air preheater.

Under these conditions the tail end system is very often the cheaper solution even though considerable additional energy costs must be accepted for reheating the flue gas /17/.

We hope that modified catalysts which have been employed recently in experimental plants will have a longer life-time. However, it is advisable to wait for longterm experiences before reliable statements can be made about the life-time of these improves catalysts /30/.

6. References

/1/ Kallmeyer, D. and König, J.: Einführung von NO_x-Minderungstechniken in mit rheinischer Braunkohle gefeuerten Kraftwerken. BWK Brennstoff-Wärme-Kraft 39 (1987), issue 5, pp. 249 - 253)

/2/ Reidick, H.: Primäre NO_x-Minderung bei Braunkohlefeuerungen. EVT-Register, issue 46 (1987), pp. 32 - 36 (EVT: Energie- und Verfahrenstechnik GmbH, P.O. Box 10 12 43, Johannesstr. 37-45, 7000 Stuttgart 10, FRG)

/3/ Biffar, W., Drews, R., Hess, K., Lehnert, R. and Scheidsteger, D.: Entstickung von Rauchgasen mit SCR-Katalysatoren. BWK Brennstoff-Wärme-Kraft 38 (1986), issue 5, pp. 211-216)

/4/ Sodec, F.: Einsatz von Aktivkoksen zur NO_x-Minderung. Lecture in "Haus der Technik", Essen, June 23/24, 1987.

/5/ Stand der Stickoxidminderung durch Sekundärmaßnahmen. VGB Kraftwerkstechnik 87(1988), issue 1, pp. 60-68

/6/ Weber, E. and Hübner, K.: Ergebnisse reaktionskinetischer Untersuchungen zur katalytischen NO_x-Reduktion mit Ammoniak. In: VGB-Handbuch "NO_x-Bildung und NO_x-Minderung bei Dampferzeugern für fossile Brennstoffe". Essen 1986/88

/7/ Bubjak, W. and Gutberlet, H.: Diskontinuierliche Ermittlung des NH_3Schlupfes durch Untersuchung des Flugstaubes. In: VGB-Handbuch /6/.

/8/ NO_x-Symposium Karlsruhe 1985 - Internationale Betriebserfahrungen.
University of Karlsruhe, february 1985

/9/ Hein, K.R.G., König, J. and Bals, M.: Problematik des Ammoniakschlupfes bei Anlagen zur NO_x-Minderung. VGB Kraftwerkstechnik 67 (1987), issue 9pp. 861-865

/10/ Bubjak, W. and Gutberlet, H.: Untersuchungen zum Eintrag von NH_3 aus DENOX-Anlagen in REA-Abwasser. VGB Kraftwerkstechnik 67 (1987), issue 9, pp. 876-883

/11/ Stäbler, K., Schönbucher, B. and Bilger, H.: NO_x-Minderung durch Sekundärmaßnahmen. VGB Kraftwerkstechnik 68 (1988), issue 7, pp. 735-743 and english issue: VGB Kraftwerkstechnik 68(1988), issue 7, pp. 652-659

/12/ Schallert, B.: Erfahrungen aus einem zweijährigen Betrieb mit DENOX-Pilot-Anlagen. VGB Kraftwerkstechnik 88 (1988), issue 4, pp. 432-440

/13/ Gutberlet, H.: Einfluß der Feuerungsart auf die Vergiftung von DENOX-Katalysatoren durch Arsen. VGB Kraftwerkstechnik 68 (1988), issue 3, pp. 287-293

/14/ Schumacher, B.: Bisherige Erfahrungen mit SCR-DENOX-Anlagen zur Stickoxidminderung. EVT-Register, issue 47 (1988), pp 27-38

/15/ Schönbucher, B., Tilch, G., Quittek, Ch.: SCR-Versuchsanlagen hinter einer Naß-REA. VGB Handbuch /6/

/16/ Hannes, K. and Eichholtz, A.: Erfahrungen der Steag AG mit Versuchsanlagen zur Stickoxidminderung. Anwendungsreport Rauchgasreinigung. VDI-Verlag 1986, pp. 84-89

/17/ Schönbucher, B. and Quittek, Ch.: Nachrüstung von DENOX-Anlagen in bestehende Kraftwerksanlagen. Sammelband VGB-Konferenz "Kraftwerk und Umwelt", pp. 151-160

/18/ Schönbucher, B. and Fritz, P.: Auslegung, Anordnung und Funktion der DENOX-Anlage für Block 7 im Kraftwerk Heilbronn. VGB Kraftwerkstechnik 67 (1987), issue 3, pp. 245-252

/19/ Schönbucher, B., Fritz, P. and Quittek, Ch.: Betriebserfahrungen mit den DENOX-Anlagen im Kraftwerk Heilbronn. Sammelband VGB-Konfernz "Kraftwerk und Umwelt 1987" pp. 65-71

/20/ Schönbucher, B.: Betriebserfahrungen mit der DENOX-Anlage des Blockes 7 im Heizkraftwerk Heilbronn der Energie-Versorgung Schwaben AG. VDI-Special: NO_x-Minderung in Rauchgasen 10 (1987), issue 10, pp. 57-61

/21/ Kister, D. and Rieche, G.: Demonstrationsanlage zur Rauchgasentstickung des Schmelzkammerkessels C im Kraftwerk Knepper C. BWK Brennstoff-Wärme-Kraft 39 (1987), issue 7, pp. 93-98

/22/ Necker, P. and Becker, J.: Auslegung, Anordnung und Funktion der DENOX-Anlage, Kraftwerk Altbach/Deizisau, Block 5, einschließlich Betriebserfahrungen. VGB Kraftwerkstechnik 67 (1987), issue 4, pp. 368-377

/23/ Necker, P.: Betriebserfahrungen mit der Entstickung im Kraftwerk Altbach/Deizisau, Block 5. VDI-Special /20/, pp. 35-42

/24/ Necker, P.: Weitere Erfahrungen mit der DENOX-Anlage in Block 5, Kraftwerk Altbach/Deizisau, nach mehr als einjähriger Betriebszeit: In: VGB-Handbuch /6/

/25/ Wahl, D.-J.: and Seibel, G.: Verringerung der Stickoxidemissionen in den kohle- und öfbefeuerten Kraftwerksblöcken der VKR mit katalytischem und nicht-katalytischem Verfahren. VDI-Special /20/, pp. 44-56

/26/ Wahl, D.-J.: Neueste Erfahrungen mit den Entstickungsanlagen der VKR. VGB Kraftwerkstechnik 67 (1987), issue 12, pp. 1198-1203

/27/ Becker, J.: High-Tech für low-dust. Energie-Spektrum (1988), issue 9, pp. 18 - 28

/28/ Barnet-Wiemer, H., Heidendael, M., Karanatsios, I. and Vijgen, H.: Analytik und Regeltechnik an einer Versuchsanlage zur katalytischen NO_x-Emissionsminderung. In: VGB Handbuch /6/.

/29/ Schallert, B., Gutberlet, H. and Wahl, D.-J.: Die Alterung von DENOX-Anlagen als Leitgröße für die Auswahl und Einsatzbedingungen in großtechnischen Anlagen. In: VGB-Handbuch /6/

/30/ Probst, K.: NO_x-Minderung in den Versuchsanlagen im Kraftwerk Franken II. In VGB-Handbuch /6/.

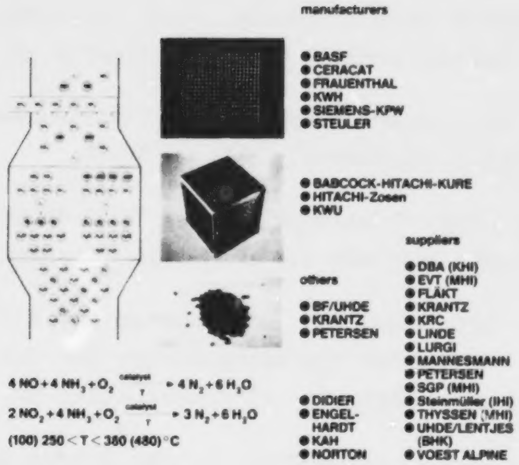


Figure 1. SCR process

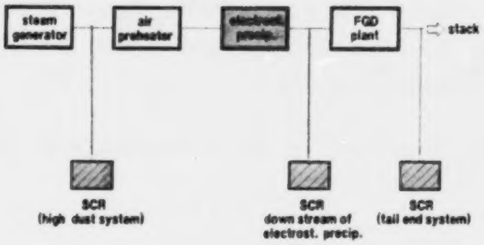


Figure 2. arrangement of a DENOX plant (SCR process)

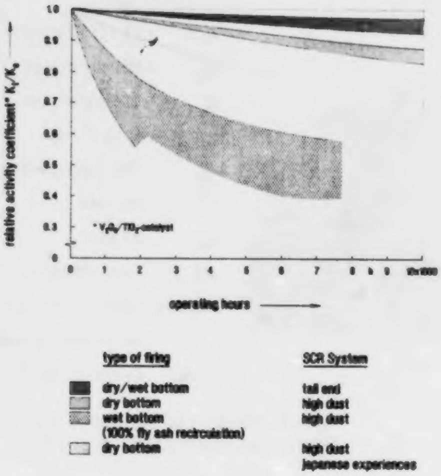
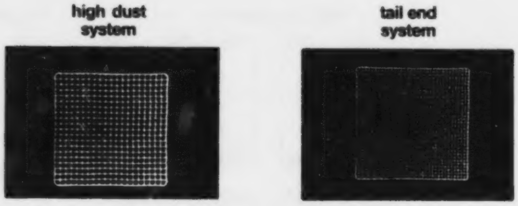


Figure 3. DENOX pilot plants in the FRG. catalyst activity



7.4–7.0	pitch	mm	4.2
430–470	surface	m^2/m^3	750
1.0	activity*	–	1.0–1.2
100	volume	%	40–50
320–400	temperature	°C	(270) 300–320
100	pressure loss	%	~180–250
12 000	life time**	h	24 000

*basis: $V_2/O_5/TiO_2$, **NH_3 slip - 5 vppm (≙ 3, 8 mg/m^3)

Figure 4. SCR catalysts for wet bottom boilers

V_{FG}	$= 2 * 1\,175\,000$ m^3/h (s.t.p., dry)
$c_{NO_x}^{in}$	≈ 800 mg/m^3 (s.t.p., dry)
$c_{NO_x}^{out}$	< 200 mg/m^3 (s.t.p., dry)
c_{dust}	$\sim 5 - 7$ g/m^3
c_{SO_2}	$\sim 1500 - 2\,500$ mg/m^3 (s.t.p., dry)
T	$= 320 - 390$°C
V_{cat}	$= 2 * 413$ m^3
pitch	= 7.5 mm, cells = 20 * 20
catalyst life	= 12 000 h, 3 years in maximum (guarantee) 16 000 - 18 000 h (expected)
NH_3 slip	$= < 5$ vppm (≈ 3.8 mg/m^3)

Figure 5. Heilbronn power station. unit 7. DENOX plant (high dust SCR system)

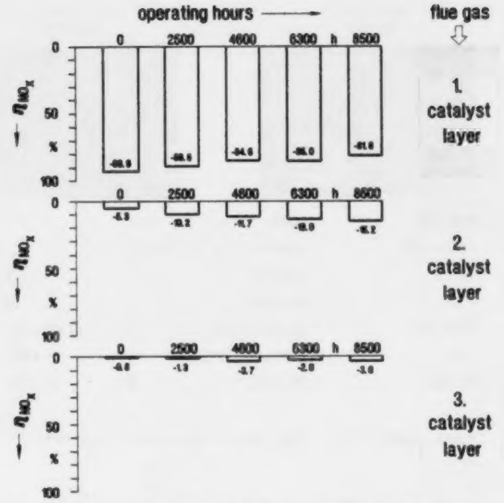


Figure 6. hard coal-fired boiler. NO_x decline across the catalyst layers for a high dust SCR system.

Table 1

properties of german hard coal

heating value (net)	MJ/kg	18 - 30
humidity	%	5 - 12
ash	%	5 - 12 (30)
volatile	%	17 - 30 (40)
sulphur	%	0.8 - 1.5
nitrogen	%	1.2 - 2.0
chlorine	%	0.1 - 0.3

Table 2

hard coal-fired boilers: flue gas composition (behind economizer)

temperature	°C	300 - 400 (420)
water	%	7 - 9
O_2	%	2 - 4
CO_2	%	15 - 17
SO_2	mg/m^3	1500 - 3500
SO_3	mg/m^3	10 - 30
NO_x	mg/m^3	650 - 800*) or 1200 - 2000**)
dust	g/m^3	5 - 12 (40)

* dry bottom firing system

** wet bottom firing system

Table 3

hard coal-fired boilers: fly ash composition

SiO_2	%	42 - 55
Fe_2O_3	%	5 - 12
Al_2O_3	%	24 - 33
CaO	%	0.5 - 8
MgO	%	0.6 - 4
Na_2O	%	0.2 - 1.2
K_2O	%	1 - 5.5
C	%	< 5

Table 4

SCR process. catalyst properties

- NO_x removal efficiency

$$\eta_{NO_x} = (c^{in}_{NO_x}, c^{ex}_{NO_x}, T_{FG}, X, AV, c_{O_2})$$

molar ratio $$X = \frac{NH_3}{NO_x} \quad [-]$$

catalyst capacity $$AV = \frac{\dot{V}_{FG}}{A_{cat}} \left[\frac{m^3(s.t.p., wet)}{h\,m^2} \right]$$

- activity $$k_1 = -\ln(1-\eta_{NO_x})\,AV \left[\frac{m}{h}\right]$$
- NH_3 slip
- SO_2 conversion rate

Table 5

Heilbronn power station. Unit 7. DENOX plant.
change of catalyst caracteristics

hours of operation	NH_3 slip	SO_2/SO_3 conversion	pressure loss (reactor)
h	vppm	%	
0	0.4	1.3	5.7
2500	0.6	1.5	6.9
4600	0.5	0.5	5.6
6300	0.5	1.4	6.3
8500	0.6	1.4	6.5

Experience Gained by Neckarwerke from Operation of SCR $DeNO_x$ Units

Dr.-Ing. Peter Necker
Esslingen

Abstract

Neckarwerke installed two SCR $DeNO_x$ units as a retrofit measure for existing power stations. Since December 1985, a high-dust $DeNO_x$ unit has been in operation in the Altbach/Deizisau Power Station, Unit 5, downstream of a boiler with dry ash removal (operating time in December 1988: 18,400 hours). In the Walheim Power Station, Unit 2 (150 MW), an SCR $DeNO_x$ unit has been operated since November 1987, also as a high-dust system downstream of a slag tap fired boiler. The operating experience gained with this $DeNO_x$ unit is discussed in this paper. The measures resulting from the operating experience are presented, in particular in the field of plant engineering and behavior of the catalytic converter. Two effects in connection with the $DeNO_x$ units - the NH_3 freight of the flue dust and the air preheater loading - which have gained particular importance for operation, are described.

1. Introduction

Neckarwerke are a regional power utility company (7.5 billion kWh/a, peak load of network 1370 MW, 6 coal-fired units, 2 interests in nuclear power stations). They operate 2 coal-fired units with SCR units to reduce the NO_x emissions.

In the Altbach/Deizisau power station, an SCR unit has been operated on Unit 5 (420 MW) downstream of a boiler with dry ash removal since 1985. At the end of December 1988, this SCR unit has been in operation for 18,400 hours. In the Walheim power station, also an SCR $DeNO_x$ unit has been operated on Unit 2 (150 MW) downstream of a slag tap fired boiler since October 1987. At the end of December 1988, this unit had 7,553 operating hours. Both units are of the high-dust SCR type. The emission limit value to be met by both units is 200 mg NO_x/m^3 (Unit 5: 6% O_2, Unit 2: 5% O_2).

Because both units are demonstration objects for introduction of the SCR technology in Germany, they are sponsored by the German Federal Environment Agency (UBA) in Berlin.

2. The $DeNO_x$ Units of Neckarwerke

Both the Altbach/Deizisau Unit 5 and Walheim Unit 2 systems were retrofitted in existing stations.

Initially, the $DeNO_x$ unit in Unit 5 had been designed so that only 80% of the flue gases were to be purified in the catalytic converter

Preceding page blank

at full boiler load (SCR partial-flow system). Fig. 1, left side, shows this circuit. A paper on the $DeNO_x$ unit /1/ and the first operating experience gained with the SCR system - which were altogether positive - (up to approx. 6,000 operating hours) was presented at the EPA/EPRI NO_x Symposium 1987 in New Orleans /2/. Further operating experience has shown that the NO_x content downstream of the boiler, i.e. upstream of the catalytic converter, depends on the coal quality used to an extremely great extent. Fig. 2, left side, illustrates this great dependence; the concentrations at the inlet into the SCR unit are between 400 mg NO_x/m^3 and almost 800 mg NO_x/m^3. Since this partial-flow system had been designed for an NO_x inlet concentration between 550 and 600 mg NO_x/m^3, the SCR unit was clearly overstrained with these high inlet concentrations with acceptable NH_3 leakage, or unrestricted use of all coal types available on the German market was not possible. Fig. 3 gives a comparison between the required separation level of a partial-flow system and that of a full-flow system as a function of the NO_x inlet concentration. If it is assumed that a separation level of 75 to 80% is the level that can be attained without special measures, this level is already reached at just under 600 mg NO_x/m^3 with a partial-flow system while a full-flow system comes up to this level at 800 mg NO_x/m^3 and above. In order to be more flexible with regard to the purchasing of coal and operation of the boiler unit, Neckarwerke therefore decided to convert the partial-flow system into a full-flow system in summer 1988. Fig. 1, right side, shows the new plant design. This configuration, with 1 start-up bypass and two reactors, has been operated since November 1988. Fig. 4 illustrates the installation layout in the boilerhouse. The alteration work made it necessary to shut down the unit in May 1988 for 3 weeks (regular inspection) and for 1 week in November 1988.

Fig. 5 shows the installation layout of the $DeNO_x$ unit at Unit 2 in the Walheim power station. The boiler - which originally had 2 flues - was altered so that the flue gases are routed upwards in a newly built flue gas duct and from top to bottom across the catalytic converter. Due to the existing two air preheaters, the entire $DeNO_x$ system has been designed with 2 ducts. NH_3 injection takes place at the beginning of the upward duct section. Of the 4 planned catalytic converter levels, 3 levels are currently equipped. In the air preheaters, the existing metal sheets were replaced by sheets which are suitable for $DeNO_x$ (enameled and easy to clean). Due to the alteration in spring 1987, the unit had to be shut down for 6 months.

3. Operating Experience

This report on the operating experience places less emphasis on results which are produced and explained with the highest degree of scientific meticulousness, but is intended to provide information on experience gained in "normal" operation, with all its constraints and shortcomings. The measures derived from that are to be presented and an indication given of how the problems can be better coped with.

3.1 Experience with Process Engineering

The NO_x reduction in SCR systems is based on the addition of NH_3 to NO_x containing flue gas in such a manner that the appropriate NH_3 molecule is available to each NO_x molecule to the largest possible extent. The NO_x/NH_3 mixture reacts at the catalytic converter to form nitrogen and water vapor. For this, the process must be designed so that these requirements can be safely met in large-scale plants under all operating conditions. This results in the following design criteria for the system:

- Adjustable NH_3 dosing (according to the required NO_x volume)
- Intimate mixing
- Satisfying the reaction conditions at the catalytic converter
- Measures to protect the catalytic converter against harmful flue gas components (e.g. dust).

Table 1 is a compilation of the chemical/physical requirements, supplemented by the possible technical measures and the interfering effects. The need to meet the requirements to an ever increasing degree rises with increasing NO_x separation level. Unit 5, the first SCR $DeNO_x$ unit in Germany on a large-scale industrial basis, can be characterized in this respect as follows:

- Difficult dosing conditions
- Extremely short mixing section
- Mixing effects by eddy flow at the shutoff dampers
- Flow homogenization by duct extension
- Favorable dust load (6 to 8 gr/m^3).

The extremely difficult conditions were able to be handled satisfactorily to a certain degree at the main reactor for separation levels of up to 75%, due to

- previous model experiments,
- two separate NH_3 injection systems, and
- some modifications and adaptations of the NH_3 nozzle diameters which were corrected several times.

For installation of the secondary catalytic converter, the conditions for dosing and mixing are solved far better - due to the experience gained from the primary catalytic converter (highly turbulent dosing range, baffling, mixing section, section for flow steadying). Figures 6 and 7 present the results from NH_3 leakage measurements downstream of the primary and secondary catalytic converters, for a separation degree of approx. 71%. The distribution of the NH_3 leakage across the flue gas duct cross section downstream of the catalytic converter can be used as a measure to indicate that the requirements have been met. The better conditions at the secondary converter result in the fact that the NH_3 leakage downstream of the catalytic converter is distributed far more evenly. A criterion for this is the standard deviation from average. The results were obtained by a specific large-scale test program.

Downstream of the secondary catalytic converter (Fig. 7), the standard deviation from the average value is 36%, and downstream of the primary catalytic converter it is 69%. It must be pointed out here that the absolute NH_3 leakage values are very low, with approx. 0.6 mg NH_3/m^3 downstream of the primary catalytic converter, and approx. 0.15 mg NH_3 downstream of the secondary converter (see Chapter 3.2).

The Walheim Station, Unit 2, is equipped with a slag tap fired boiler. 30% of the German boiler plants have this type of firing which produces very high NO_x emissions. These are generally between 1200 and 2400 mg NO_x/m^3. Before the NO_x reduction measures were installed in 1987, Unit 2 in Walheim had emission values between 1900 and 2200 mg NO_x/m^3 - depending on the coal type used (Fig. 2, right side). For this reason, primary and secondary measures had to be taken to attain the limit value of 200 mg NO_x/m^3. By installing multi-stage mixing burners supplied by Steinmueller as a primary measure, the NO_x values downstream of the boiler were reduced to 1100 to 1600 mg NO_x/m^3 - depending on the coal type. This meant that a separation level of 82 - 87% was required for the secondary measure! For such extreme separation levels, special emphasis had to be placed on an optimum NH_3 dosing (20 nozzle systems with separate external adjustment feature), long mixing section, baffles and even flow distribution. Fig. 5 shows the solution found for installation from compliance with these requirements. Special mention is made of the constant pressure distribution upstream of the rectifier level. The necessary separation levels of approx. 85% are attained by these measures with extremely low leakage rates. The NH_3 leakage rates are 0.15 mg NH_3/m^3 after approx. 6,600 hours. NO_x and NH_3 profile measurements across the flue gas cross section resulted in standard deviations of 30% for NO_x and 19% for NH_3 - referred to the average value. At the present time, only 3 catalytic converter levels are equipped.

The experience gained from operation of Unit 5 was fully taken into account in the design of the $DeNO_x$ system in Unit 2 of the Walheim power station, and it thus created the conditions for troublefree operation of Unit 2.

3.2 NH_3 Concentration at Flue Dust

The NH_3 deposits at the flue dust have proven to be the crucial problem for the operating characteristics of the $DeNO_x$ system at Unit 5 in the Altbach/Deizisau power station. As the further measures can be better understood when this operating problem is known, this item is dealt with first in the description of the operating experience.

In the order placed for the DeNO$_x$ system, the NH_3 leakage downstream of the catalytic converter was specified at max. 5 vpm (= 3.8 mg NH_3/m^3) as the guaranteed value during the catalytic converter life. This procedure was based on information, recommendations and "experience" of the licensors of the German plant suppliers. Own operating experience and findings were not yet available in Germany. The acceptance of these "guaranteed values" has proven to be an error from the point of view of the plant operator; this value is too favorable for the suppliers.

For disposal of the fly ash separated off in the electric filter, Neckarwerke have entered into an agreement with a large cement mill. Since the fly ash has pozzolanic properties, a share of approx. 22% fly ash can be added to the fired cement clinker; thus producing a fly ash cement with specific properties. If the NH_3 concentration in the flue dust exceeds a defined value, this may result in a release of NH_3 during concrete mixing (i.e. wetting) due to the alkaline characteristics of the cement and, thus, to a noticeable smell. Depending on the intended purpose and type of use, we believe that 100 mg NH_3/kg fly ash - without special treatment of the fly ash - is a certain limit value of the NH_3 concentration. For 60 mg NH_3/kg and above, special conditions apply for disposal. If the NH_3 content of the fly ash jeopardizes the utilisation of the flue dust and, thus, waste disposal of a power station, and this is caused by the DeNO$_x$ system, this problem must be carefully studied. Own tests have shown that the concrete properties are not altered by these effects.

Neckarwerke use relatively high-quality hard coal types, with an ash percentage of 6 to 8%. Initial information from the years 1984/85 and 1986 /4/ on the path the NH_3 leakage takes showed the distribution given in Fig. 8, top; i.e. approx. 70% of the NH_3 leakage are emitted via the fly ash. Mathematically speaking, on this basis the use of a coal with 7% ash and an NH_3 leakage of 1.4 vpm (= 1.0 mg/m^3) results in approx. 100 mg NH_3/kg, and a leakage of 5 vpm (= 3.8 mg/m^3) in approx. 350 mg NH_3/kg.

During 10 test series that were carried out in the meantime and took approx. 1 week each, an NH_3 depositing rate on the flue dust of 70% was not able to be reproduced. The vast majority of measured values is clearly below this. Fig. 9 illustrates the results obtained by the 10 test series. The low deposition rates on the flue dust are partly combined with very high separation levels and the corresponding higher leakage.

The results presented on the bottom of Fig. 8 were found by a test series that was specially aimed at pinpointing the NH_3 leakage. A clearly measurable NH_3 volume flow of up to 50% of the NH_3 leakage could be detected in the heated combustion and mill air flow /6/. The NH_3 deposition rate on the flue dust was around 50%. Further, an NH_3 deposition on the air preheater of 10% could not be verified. Based on long-term observation of the air preheater in connection with air preheater washing, values of clearly < 5% must be assumed (see Chapter 3.4). With these test results, the incongruity /3,5/ in the analysis of the NH_3 leakage which could be recognized since 1986 was able to be explained by the NH_3 transfer from the flue gas side to the air side in the air preheater. It must however be emphasized at this point that these statements are subject to relatively high tolerances because the measurements were carried out on a large-scale plant. It is extremely difficult to maintain all parameters of influence constant over the extremely long test period required for such tests (desirable are > 8 hours). Fig. 10 shows an example of the effect reproduced repeatedly during these test series, i.e. that the NH_3 concentration on the flue dust increases over the test period under constant load (increase by approx. 15 to 30%) /7/.

On the basis of the above experience, we now design the catalytic converters for an NH_3 leakage of 2 vpm (= 1.5 mg NH_3/m^3). However, we wish to warn against an oversizing of the catalytic converters, because high converter volumes (= low S_v velocities) lead to an increase in the SO_2/SO_3 conversion rate, thus creating fresh problems.

Concerning Unit 2 in Walheim, generally speaking it can be stated that the leakage values are still very low, due to the process optimization for mixing and the operating time of 6,000 hours. The NH_3 values on the flue dust are therefore between 10 and 20 mg NH_3/kg.

While parameters such as boiler load, ash percentage and calorific value of the coal were constant or corrected in the above correlations between NH_3 leakage and NH_3 concentrations on the flue dust, Fig. 11 gives a result of the NH_3 concentration on the flue dust as obtained in "normal" operation of Unit 5 since its startup in December 1985, subject to all the ups and downs of everyday operation. During the first six months (up to about June '86), the NH_3 content of the flue dust was not given the importance it now has; rather the optimization and improvement measures on the plant played the main role. This was followed by the phase of introduction of analytic chemistry in the plant laboratory which is shown by some uncertainty of the test results (July to August 1986). If the results of the test campaigns, for which extreme situations were created intentionally for the plant, are not taken into account, the measurement results of the NH_3 concentration on the flue dust can be put down to some trend curves: first the increase in NH_3-concentration between September 1986 and April 1987, then the phase during which the NH_3 dosing was reduced to limit the NH_3 concentration in the flue dust (May to December 1987), followed by two phases with rising NH_3 concentrations in the flue dust. These four phases exactly illustrate the history of the Unit 5 $DeNO_x$ system, the operating experience with the catalytic converter and the conclusions drawn.

3.3 Catalytic Converter Behavior

3.3.1 Catalytic Converter Behavior in Unit 5

Part of the catalytic converters in the $DeNO_x$ system of Unit 5 have been in operation for 18,400 hours till December 1988. Fig. 12 gives the activity curve of these catalytic converters. It can be clearly recognized that the actual activity decrease was below the value on which the design of the system was based. Dust deposits, blockage or erosion phenomena could not be found. Therefore, the function of the catalytic converter can be fully confirmed.

A decreasing activity is characterized by the fact that the NH_3 leakage increases with constant separation efficiency. This continuous increase in the NH_3 leakage over the period of operation also becomes apparent by the increase in the NH_3 concentration on the flue dust in Fig. 11. This trend manifests itself in different ramps. Until May 1987, a first increase takes place - the result of the decrease in activity which can be recognized in Fig. 12 up to approx. 8,000 operating hours. It began to show that the critical NH_3 concentrations on the flue dust would be reached. It must be pointed out that the NH_3 leakage of 2 mg NH_3/m^3 downstream of the catalytic converter was still far below the guaranteed value at this point in time. On the basis of the load forecasts for 1988, we decided in autumn 1987 to

- equip the third layer with a new catalytic converter in December 1987, and to

- convert the system into a full-flow $DeNO_x$ system in May.

According to the operating experience after approx. 10,000 hours in autumn 1987 - which gave no indication of problems with dust erosion, blockage and deposits -, we decided to use catalytic converters with a reduced web thickness (instead of 1.4 mm now 1.05 mm; increase in inner surface + 16%) for the new equipment. This improvement resulted in a reduction of the NH_3 concentration in the flue dust, at the same time maintaining the limit value of 200 mg NO_x/m^3 (since January '88). After this, again an increase in the NH_3 concentration in the flue dust due to the activity decrease in the catalytic converter was found. The catalytic converters with the smaller subdivision have stood the test.

In May 1988, the reactor bypass ducts were shut off during the annual Unit inspection so that the secondary catalytic converter could be installed. From May to November 1988, the flue gas was passed solely through the reactor. Thus, the reactor was overloaded by 25% at 100% boiler load when compared with the original design. During the shutdown in May, the rectifier level installed in the reactor was equipped with a catalytic converter level which consisted of the catalyst bars which were removed in December and split into halves over their length. With this measure, the remaining residual activity of the removed catalytic converters was utilized and the activity of the reactor increased with regard to the overload operation. The success of this measure manifests itself in the decrease of the NH_3 concentration in June. The activity decrease of the catalytic converter, in turn, can be discerned by the rising NH_3 concentration in the flue dust. Visual inspections of the catalytic converter level used as a rectifier level have justified this risky enterprise. The erosion effects on the "rectifier catalytic converters" are extremely small. In November, the ducts to the newly installed secondary reactor were opened, thus reaching the ultimate stage. The first and second levels of the secondary reactor are equipped with the remaining catalytic converters from the third layer of the main reactor which was removed in December 1987, and the third level with new catalytic converter modules. The success of this measure manifests itself in the NH_3 concentration values of the flue dust since December 1988.

Fig. 13 presents a summary of the effects of the different measures on the available relative overall activity of the catalytic converter, referred to the initial activity and inner specific surface. In order to understand the relationship between the measure taken and the influence on the NH_3 flue dust concentration better, the ordinate was drawn at the same scale as in Fig. 11 on top. The figure shows: at the end of 1987 activity increase by new catalytic converter layer with larger inner surface; in May 1988 increase by installation of half the used catalytic converter layer; in November 1988 increase by opening the secondary catalytic converter.

During the activity tests on the catalytic converter modules, a strong divergence was found in the results of the different test institutes (Fig. 12, at 11,200 hours). Standard tests with 300 mm long sections from the start and end of the 1 m long catalytic converter bar give different results than the test of five 20 cm long sections. Fig. 14 illustrates this relationship and indicates that the procedure for the activity measurement must be defined very carefully - in particular because it is a matter of guaranteed values.

The operating experience gained from the 18,400 operating hours of the catalytic converters at Unit 5 and the resultant measures can be summarized as follows:

- The activity decrease of the catalytic converters is smaller than the value that formed the basis of the design.

- No erosion problems arose at the catalytic converters; therefore, the web thickness was reduced during the first catalytic converter replacement.

- The replacement of the rectifier level by catalytic converter modules did not result in an additional erosion problem with the dust load occurring and the given flow conditions; therefore, the rectifier level can be eliminated.

Comprehensive measurements on the formation of N_2O gave values of less than 5 mg/m^3 upstream of the catalytic converter and 3 mg/m^3 downstream of it. The effect of a reduction of the N_2O concentration downstream of the catalytic converter could be proven in both $DeNO_x$ units.

3.3.2 Catalytic Converter Behavior in Unit 2

Unit 2 of the Walheim Power Station is equipped with a slag tap fired boiler. Before the NO_x reducing measures were introduced, the entire flue dust caught in the E filter was fed back into the furnace, molten in the furnace body and drawn off from the furnace as granulated material (Fig. 15). The coal contains a multitude of trace elements which are released during the combustion process, among others As. As is identified as a catalytic poison. Since As evaporates at the temperatures in the boiler furnace body and is therefore not removed together with the granulated material, but condenses at the flue dust in the flue gas path when the temperatures decrease, the As is concentrated in the flue gas due to the flue dust feedback to the boiler in the case of slag tap fired boilers. As becomes a catalytic poison, in particular, when it is in the gaseous phase in the flue gas. With the high-dust arrangement of SCR systems directly downstream of the boiler, there is a risk of the catalytic converter becoming desactivated prematurely by the As. This danger to the catalytic converters can be countered in two different ways:

- Reducing the As concentration by interrupting the full flue dust feedback

- Moving the SCR system to downstream of the flue gas desulphurization plant.

In /8/, the installation of the SCR system downstream of flue gas desulphurization plants is described in detail. At Unit 2 in the Walheim power station, Neckarwerke decided on the high-dust arrangement for the SCR system. This decision included the equipment for flue dust removal. Detailed tests have shown that this measure allows the As content of 4 mg As/m^3 (gaseous) - which is very low in this system - to be reduced down to 1 mg As/m^3. The overall As concentrations (gaseous and bound to fine dust) are in the range of 365 mg As/m^3 without removal (corresponding to a concentration in the dust of 4,900 mg As/kg), and 87 mg As/m^3 (corresponding to 1,000 mg As/kg) with removal. Further, it could be determined by measurements that the highest possible removal during soot blowing is particularly effective for a reduction of the As content in the flue gas (As concentrations up to 2,000 mg As/m^3). These measurements were verified by As analyses of the flue dust deposits in the boiler (As concentrations 5,000 up to max. 20,000 mg As/kg).

These measures (approx. 10% removal during normal operation; 100% removal during soot blowing) apparently prevented the suspected rapid catalytic converter poisoning. Fig. 16 shows the course of the activity reduction in comparison to the design values. Here, too, the actual activity reduction is smaller than was assumed in the design. It must be noted that - contrary to the catalytic converters at Unit 5, the activity reduction at the catalytic converters in the Walheim power station is different at the various levels. Here, the activity reduction on level 1 is clearly stronger than on levels 2 and 3; a certain As catcher effect is attributed to the first level.

3.4 Air Preheater Washing

In earlier reports /1,8/, only test washing cycles at minor sectors of the air preheater were described; in 1988, 2 full washing cycles of the air preheater became necessary due to the rising pressure drop. During the washing operations, the NH$_3$ that was stored in the air preheater over the operating period comes out again in concentrated form. Air preheater sheets (easy to clean, middle and end layer enameled) that are suitable for $DeNO_x$ are installed in both systems. The installed air preheater blowing device is operated once a day.

Fig. 17 gives the course of the NH_3 concentration during the individual washing operations for the test and full washing cycles performed. The presentation of the test washes clearly shows that the NH_3 settles in the air preheater to an increasing extent over the operating period. The rapid decrease in concentration indicates that the ammonium salts are easily soluble. For the full washes, the washing cycles could no longer be distinguished as strictly, but distinction was only made into preliminary washing, main washing and rinsing. Here, too, it can be seen that the waste waters with a high NH_3 charge can be separated off at the beginning for disposal and that the higher volume of washing water only has a small charge. Approx. 1200 to 1400 m^3 of washing water were needed for the full washes. The NH_3 quantities contained could be estimated from the NH_3 concentrations and washing water volumes. The quantities are given in Fig. 17 with the corresponding operating times. From these figures, the deposit figures for the air preheater used in Chapter 3.2, Fig. 8, can be estimated. Concerning the second full wash, it can be stated that this was not caused by a defective $DeNO_x$ unit (relatively small NH_3 deposit), but that the fault must be blamed on the operation of the calorifer or air preheater blowing device.

Analyses of the air preheater washing water resulted in the fact that the ion balance between the sulphate ions and the cations found is not balanced. This leads to the conclusion that a large part of the SO_3 anions contained in the flue gas is directly absorbed by the flue dust.

The following measures were based on the operating experience with the air preheater:

- Daily blowing of the air preheater, under careful observation of the pressure drop and the function of the blowing device

- For necessary air preheater washes:

- Separation of the rinsing water into a batch with high NH_3 concentration and one with low NH_3 concentration

- Provision of appropriate storage volumes for collection of the rinsing waters.

4. Summary

4.1 In the Altbach/Deizisau Power Station, Unit 5 (420 MW_{net}, boiler with dry ash removal), the high-dust SCR $DeNO_x$ system was converted from a partial-flow system into a full-flow system.
In the Walheim Power Station, Unit 2 (150 MW), also a high-dust SCR system was installed downstream of a slag tap fired boiler. In the extension of the Unit 5 system and in the new building of Unit 2, the

operating experience gained with the partial-flow system in Unit 5, i.e.:

- finely adjustable NH_3 dosing in an optimized flue gas flow,

- well designed long mixing sections with baffles and constant pressure distributors,
- careful design of the flow upstream of the catalytic converter, without the formation of dust streaks,

was taken into account by design measures.

4.2 The NH_3 charge of the flue dust increasing over the operating time has proven to be an important factor for operation of the power station in connection with the $DeNO_x$ system. Based on this knowledge and the strong dependence of the NO_x concentration upon the coal types used, the system of Unit 5 was extended into a full-flow system. For this, a special catalytic converter replacement method was employed. This measure allowed the NH_3 charge of the flue dust to be reduced to values between 20 and 30 mg NH_3/kg. The low flue dust concentration of approx. 6 to 8 g/m^3 at Unit 5 must be noted.

4.3 In December 1988, the catalytic converters at Unit 5 have been in operation for 18,400 hours and those at Unit 2 for approx. 7,500 hours. The decrease in activity was lower in both cases than that used as the basis for their design. The As poisoning of the catalytic converter expected due to the slag tap furnace in Unit 2 did not occur, due to the removal of the fly ash (in particular during soot blowing).

No erosion or blocking effects due to the fly ash were found in either system.

4.4 After approx. 16,800 operating hours, the air preheater in Unit 5 had to be washed for the first time. The deposits could be easily removed with water. The first washing water batches had a high NH_3 content.

4.5 Altogether, it can be stated that SCR $DeNO_x$ systems can also be operated at limit values of 200 mg NO_x/m^3, if the following is observed:

- Design requirements in the plant design;

- Correct interpretation of the supervision results; and

- Early taking of appropriate measures.

However, the efforts and measures are considerable.

List of References

/1/ **Necker, P. and J. Becker:**
Auslegung, Anordnung und Funktion der DeNO$_x$-Anlage Block 5 einschließlich Betriebserfahrungen; VGB-Sondertagung "Neue Steinkohleblöcke am Neckar", Stuttgart 1986; VGB Essen 1986

/2/ **Necker, P.:**
Operating Experience with the SCR DeNO$_x$Plant in Unit 5 of the Altbach/Deizisau Power Station; Section No. 5A-Z; Joint Symposium on Stationary Combustion NO$_x$ Control; EPRI/EPA, New Orleans, 1987

/3/ **Necker, P.:**
Weitere Erfahrungen mit der DeNO$_x$-Anlage im Block 5, Kraftwerk Altbach/Deizisau nach mehr als einjähriger Betriebszeit; Sammelband VGB-Konferenz "Kraftwerk und Umwelt 1987"; VGB Essen 1987

/4/ **Reidick:**
DeNO$_x$-Anlagen, Mitteilungen der EVT Stuttgart 1986, and some Japanese Sources, 1985 and 1986

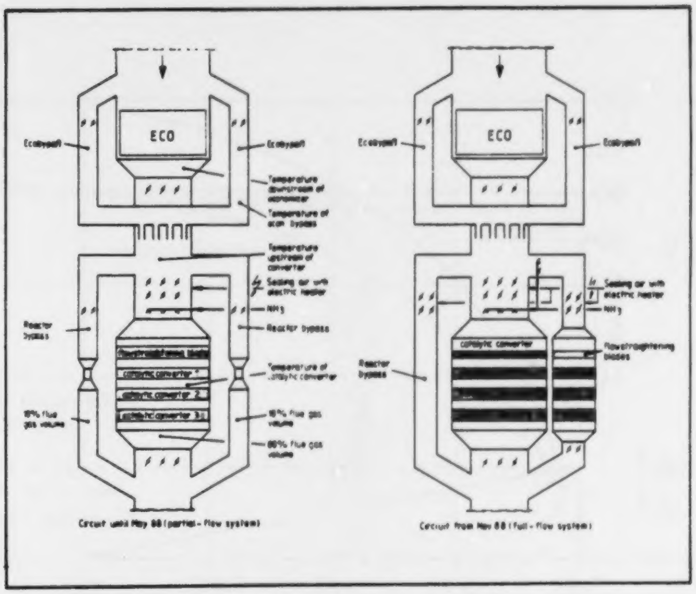
/5/ **Bujak, W and H. Gutberlet:**
Untersuchungen zum Eintrag von NH$_3$ aus DeNO$_x$-Anlagen in REA-Abwasser; Sammelband VGB-Konferenz "Kraftwerk und Umwelt 1987"; VGB Essen 1987

/6/ **Wurz, O.:**
Bericht NH$_3$/NO$_x$-Messungen am Block 5 der Neckarwerke Elektrizitätsversorgungs-AG Esslingen, Dezember 1988

/7/ **Lehmann:**
Messungen an der DeNO$_x$-Anlage Block 5; Studienarbeit; Institut für Industriebetriebslehre und Industrielle Produktion; Universität Karlsruhe; Karlsruhe 1989

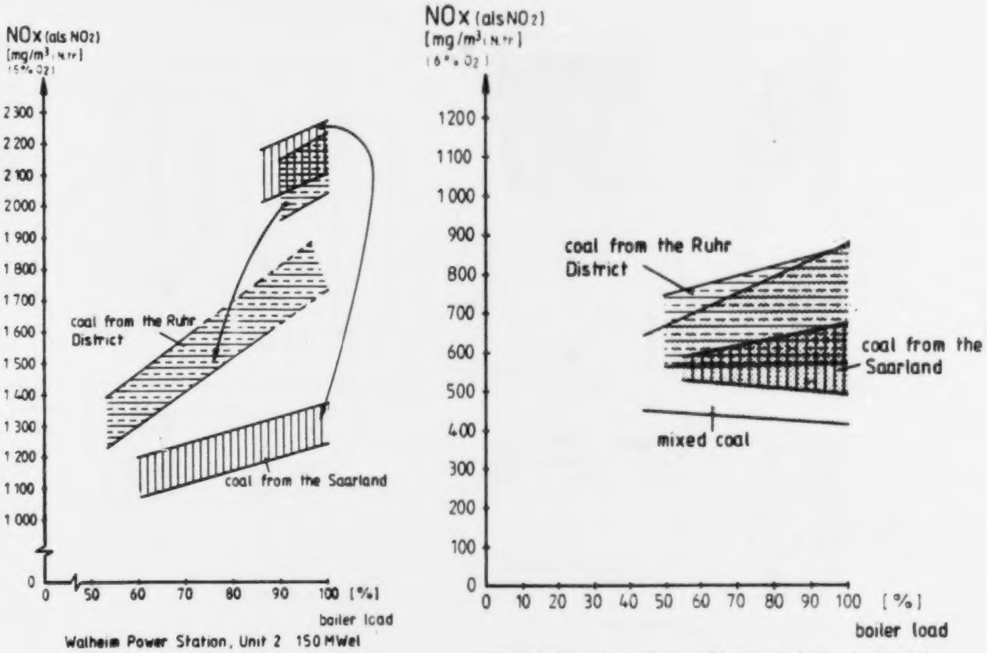
/8/ **Schönbucher, B.:**
Reduction of Nitrogen Oxides from Coal-Fired Power Plants by Using the SCR Process - Experiences in the FRG with Pilot and Commercial DeNO$_x$ Plants; EPA/EPRI 1989 Joint Symposium on Stationary Combustion Control; San Francisco 1989

/9/ **Necker, P.:**
Betriebserfahrungen mit der DeNO$_x$-Anlage im Kraftwerk Altbach/Deizisau Block 5; VDI-GET-Tagung, Februar 1988, Hannover; VDI-Verlag Essen


ECO
Ecobypaß
Ecobypaß
Temperature downstream of economizer
Temperature of econ bypass
Temperature upstream of converter
Sealing air with electric heater
NH3
Reactor bypass
Reactor bypass
Flowstraightening blades
catalytic converter 1
catalytic converter 2
catalytic converter 3
Temperature of catalytic converter
10% flue gas volume
10% flue gas volume
90% flue gas volume
catalytic converter
Ecobypaß
Ecobypaß
Sealing air with electric heater
NH3
Reactor bypass
Circuit until May 88 (partial-flow system)
Circuit from Nov 88 (full-flow system)

Shematic drawing of flue gas path
of the SCR De NO_x system
Altbach/Deizisau Power Station, Unit 5

Fig.1

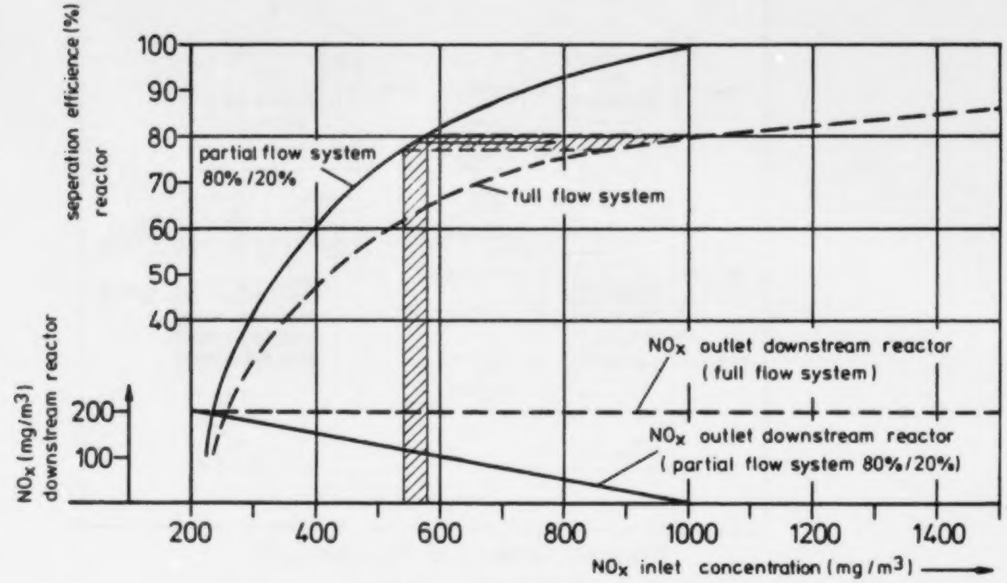


Walheim Power Station, Unit 2 150 MWel

Altbach/Deizisau Power Station, Unit 5 460 MWel

Influence of coal type on the NO_x
concentration at the boiler outlet

Fig.2



Seperation efficience by NO_x outlet concentration 200 mg/m^3
partial flow system / full flow system

Fig. 3

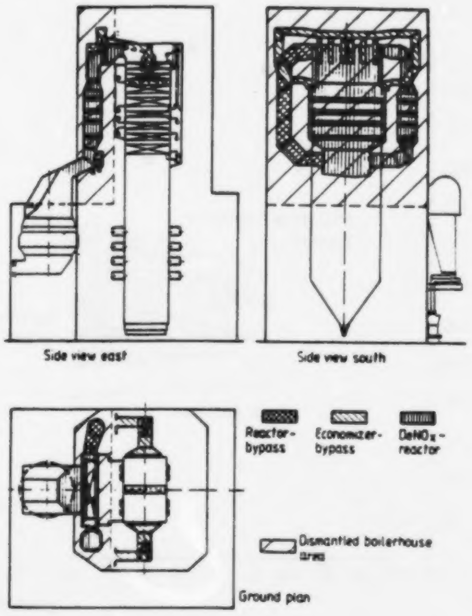


Fig. 4 Installation situation $DeNO_x$ Plant
Altbach/Deizisau Power Station Unit 5

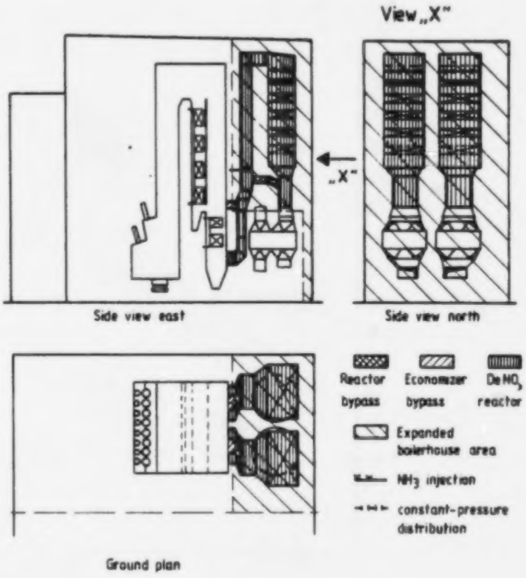
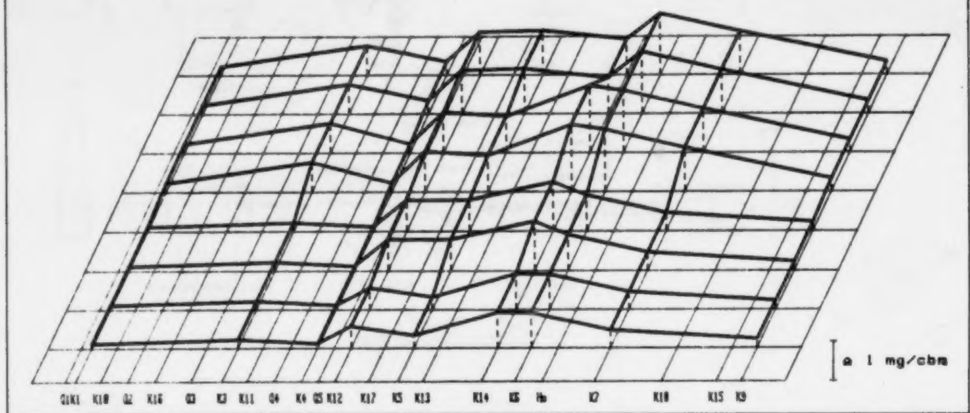
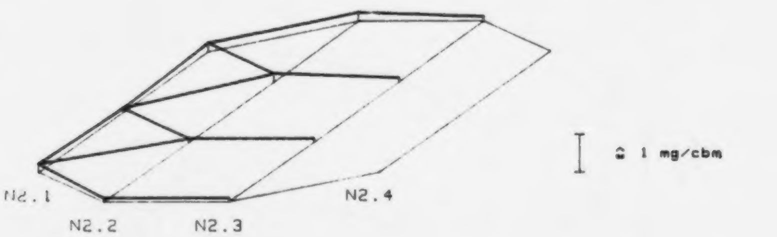


Fig. 5 Installation situation De NO_x Plant
Walheim Power Station Unit 2



NECKARWERKE ABT. UMWELT DeNOx-Meßprogramm	NH_3 measurements; test on Dec.14,1988 Primary catalytic converter	Kessel: 93 % Kat: 93 % ETA-Kat: 71 % Stöchf.: .68 Saarkohle $\bar{x}$= .661 S= .45 (68%) ung. Angaben in mg/cbm i.N.

Fig.6



NECKARWERKE ABT. UMWELT DeNOx-Meßprogramm	NH_3 measurements; test on Dec.14,1988 Secondary catalytic converter	Kessel: 93 % Kat: 93 % ETA-Kat: 71 % Stöchf.: .68 Saarkohle $\bar{x}$= .154 S= .0567 (37%) ung. Angaben in mg/cbm.i.N.

Fig.7

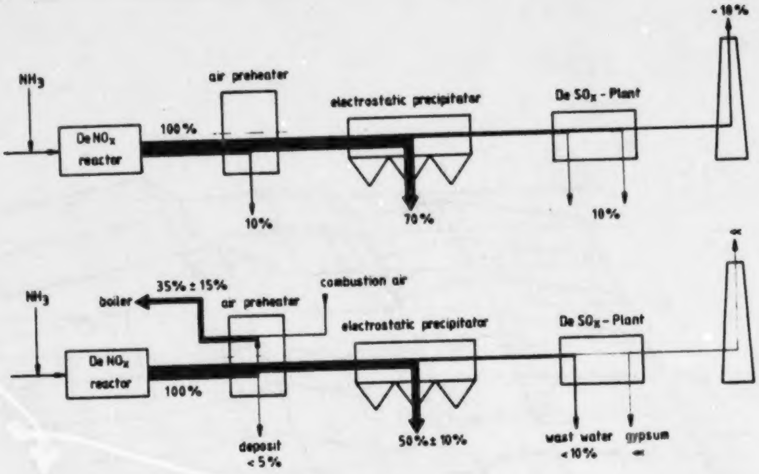
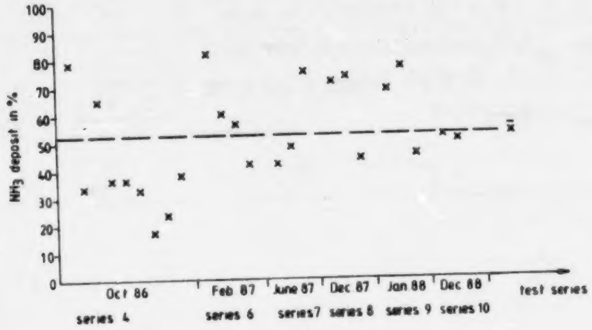


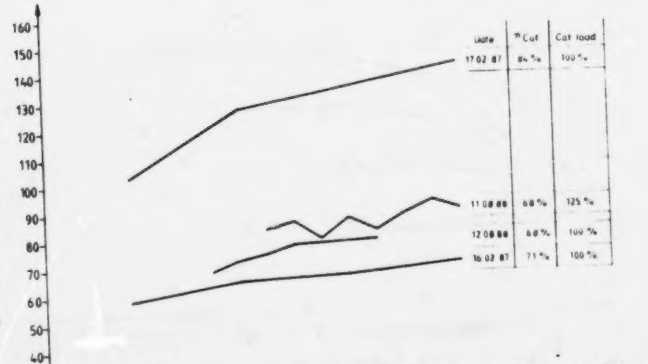
Fig. 8

Balance NH_3 leakage



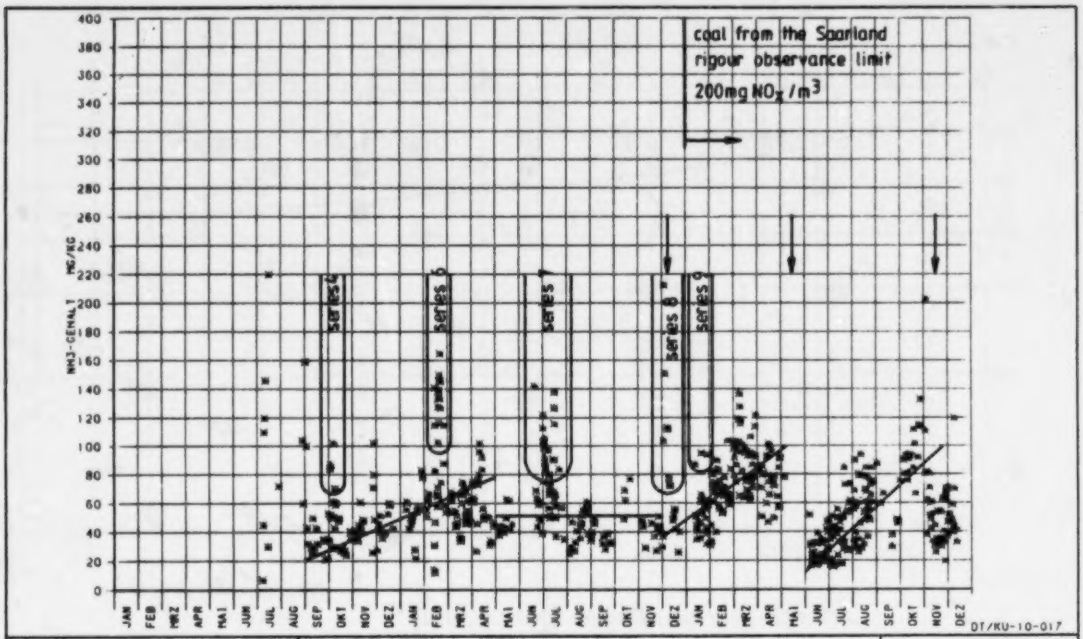
NH_3 deposit on flue dust, in per cent of the NH_3 leakage

Fig. 9



NH_3 concentration in flue dust over the daily operating period with constant boiler load

Fig. 10



NECKARWERKE
Elektrizitätsversorgungs-AG
ABTEILUNG UMWELT

NH_3 concentration in flue dust over the operating period of the SCR De NO_x system
(load > 90 %)

NH3-GEHALT

Fig. 11

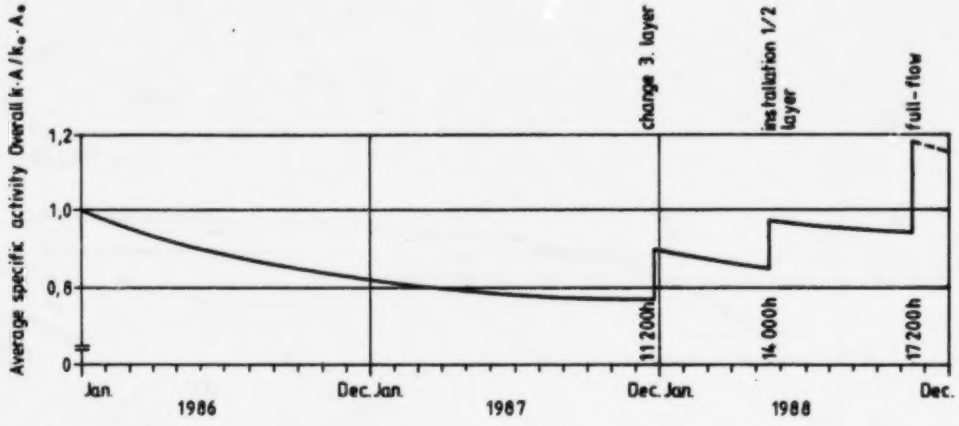
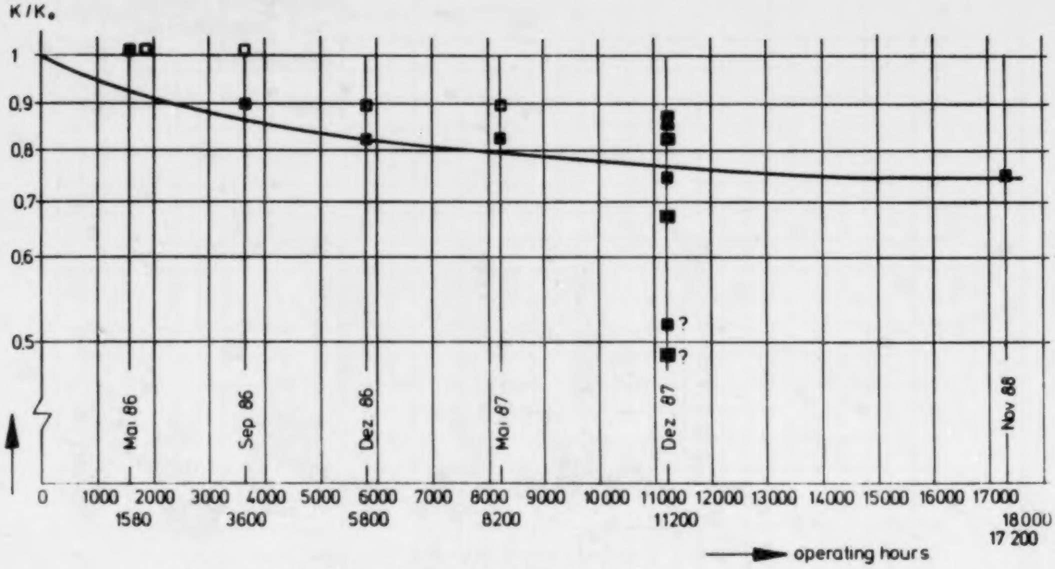


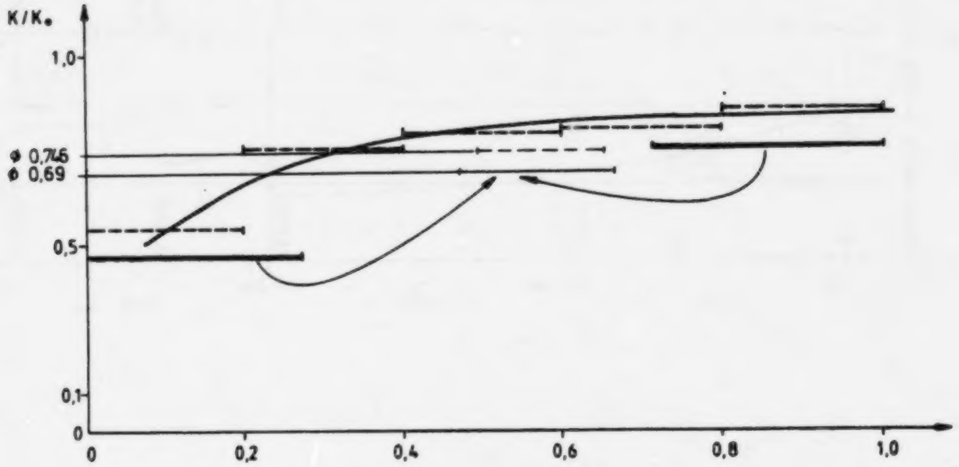
Fig. 13

Average specific catalytic converter activity
Overall reactor, Unit 5
(referred to catalytic converter at outlet)



Altbach-Deizisau Power Station, Unit 5
Results of catalytic converter activity measurements

Fig. 12



Results of catalytic converter activity measurements over the bar length
Fig. 14 Altbach/Deizisau Power Station, Unit 5

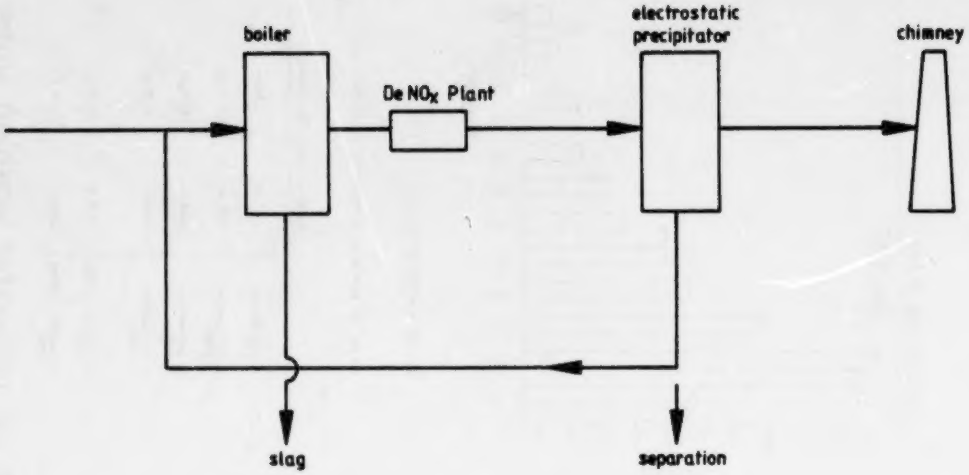
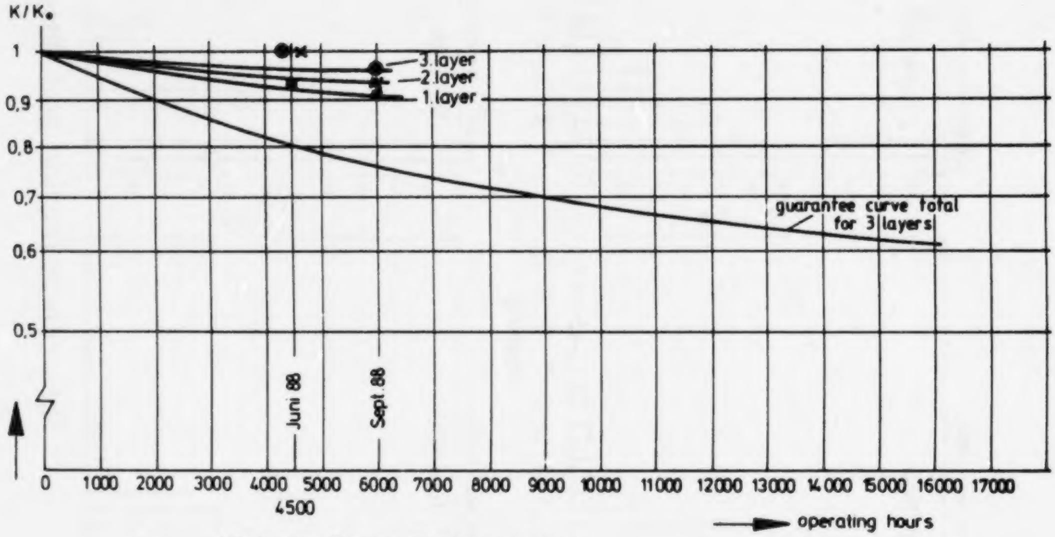
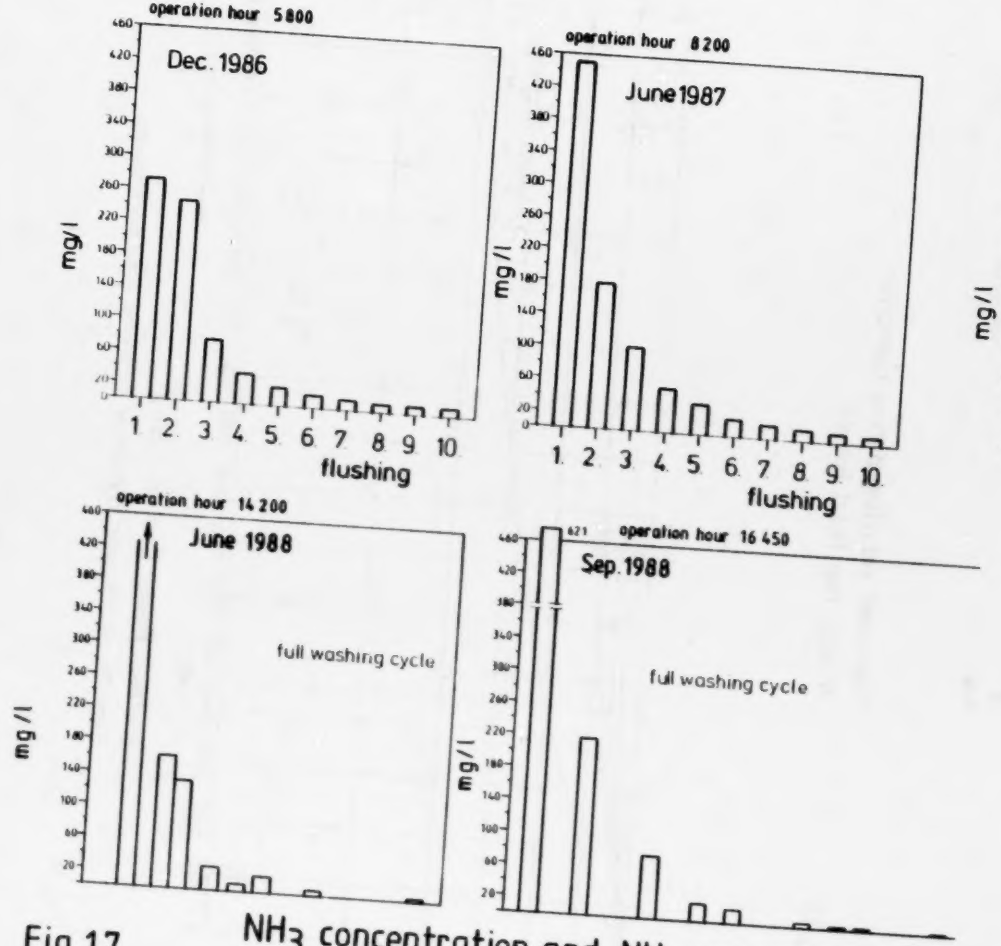


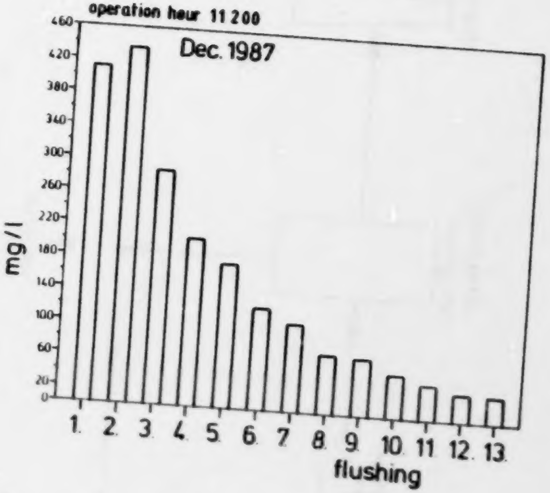
Fig. 15 Flue dust recycling during operation of slag tap fired boilers



Walheim Power Station, Unit 2
Results of catalytic converter activity measurements

Fig. 16





NH_3-loading of the air-preheater

420 MW Plant with an air-preheater of inc. 86 000 m² area

	operating hours	NH_3-loading
1. Test-washing 5/86	1417 h	6,06 kg
2. Test-washing 12/86	5800 h	30,30 kg
3. Test-washing 6/87	8200 h	38,00 kg
4. Test-washing 12/87	11200 h	90,00 kg
1. Complete washing 6/88	14200 h	180,00 kg
2. Complete washing 9/88	16450 h	45,00 kg

Fig.17 NH_3 concentration and NH_3 measurements in air preheater washing water

RECENT DEVELOPMENTS IN THE SCR SYSTEM AND ITS OPERATIONAL EXPERIENCES

H. Kuroda
I. Morita
T. Murataka
Kure Works of Babcock-Hitachi K.K.
Kure, Hiroshima, 737, Japan
Dr. F. Nakajima
Dr. Y. Kato
Kure Research Laboratory of Babcock-Hitachi K.K.
Kure, Hiroshima, 737, Japan
Dr. A. Kato
Hitachi Research Laboratory of Hitachi Ltd.
Hitachi, Ibaragi, 319-12, Japan

ABSTRACT

In the previous EPRI/EPA Joint Symposia held in Denver, Colorado in 1978 and 1980, we were honored to present our NOx removal system.

Since then, regulations for NOx emissions have become more stringent in the light of growing industrialization and its environs, bringing about great numbers of Selective Catalytic Reduction (SCR) systems in Japan, Europe and the USA. Having been awarded 30 plants for gas firing, 27 for oil firing, 20 for coal firing and 5 miscellaneous plants, approx. 80 % of which were awarded within the last 8 years. These SCR plants were not only for dry bottom boilers but also wet bottom boilers, fluidized bed boilers, heat recovery steam generators in cogeneration systems, diesel engines, iron & steel plants etc.

At this 1989 Joint Symposium we wish to introduce the progress and development of technology on SCR systems during these 8 years and then briefly present one of the newly developed technologies, namely the catalyst resistant to Arsenic.

INTRODUCTION

In Japan stringent Ambient Air Quality Standards and Emission Regulations were put in force in the 1970s because air pollution went from bad to worse due to rapid expansion of industrialization.
The emission regulations stipulated for the large stationary sources, such as big factories and thermal power stations, were so stringent that the pollution control systems have been installed one after another in both retrofit and new plants.
The SCR system were firstly developed in Japan after extensive research and put into worldwide commercial usage.
In the other industrialized countries such as the Federal Republic of Germany (FRG), the USA etc. the air pollution situation has become serious and many SCR systems came to be installed as the emission regulations tightened in such countries.

In the USA the first demonstration plant of a SCR system for a boiler plant was installed in 1982. However, other installations in boiler plants did not follow simultaneously.

Several years later the increasing demand for SCR systems started in a different field from that of conventional boilers.
Owing to PURPA (the Public Utility Regulatory Policies Act) the construction of a cogeneration plant which produces electricity and steam for multipurpose utilization instead of conventional boilers has become commonplace.
Moreover, many SCR systems for cogeneration projects have been taken up in the state of California, where NOx emission regulations appear to be particularly stringent in the USA.

In FRG when the NOx emission regulation was stipulated, the installation of SCR systems started with coal fired boiler plants, because coal is the predominant fuel in thermal power plants.
Before its installation a delegation(13 people) from the state of Baden Württemberg first visited Japan in October, 1983 for an investigation of SCR systems and a lot of delegations followed, resulting in certain license or cooperation agreements between the companies in both countries.

In general the SCR technology developed in Japan has been applied in the FRG without much difficulty. Only one matter which we had not experienced in Japan and had to develop was the NOx removal from flue gas from a slag tap boiler, a kind of wet bottom boiler.
Afterwards, this will be described more as an example of one of our developments.

HISTORY OF DEVELOPMENT AND OPERATIONAL EXPERIENCES

History of development

Fig. 1 shows the development of the Babcock-Hitachi DeNOx Process.
We commenced studies for NOx removal from exhaust gases in 1963, conducted hundreds of catalyst screening tests, life tests and optimum process studies, then began to install pilot plants in the field in 1973. At this early stage of development we had conducted a great deal of pilot tests together with laboratory tests.

As we already introduced the history of our early development at the previous EPRI/EPA Joiny Symposia (1), (2) held in Denver in 1978 and 1980, we hereby describe the further development since then.

The needs of SCR plants for retrofit utility boiler plants have rapidly increased in Japan and almost all SCR plants for retrofit boilers were installed during the first half of 1980s. Since then its demands are mainly for new utility boiler plants.

In the USA the first SCR system for a cogeneration plant which was supplied by Babcock & Wilcox Co. under the license of Babcock-Hitachi K.K. has been successfully operating since early 1986.

In Europe we have conducted about 20 pilot tests in FRG, Austria, Denmark and Sweden since 1984 in cooperation with our licensees, Uhde/Lentjes, Babcock Energy Ltd., Fläkt, and Voest Alpine as a consortium partner through which our catalyst and SCR systems were demonstrated and proven applicable for commercial use. However, while the SCR systems developed in Japan were applied to boiler plants in FRG, we encountered one problem, which had not been experienced in Japan.

Rapid deactivation of DeNOx catalysts was observed only in a slag tap boiler with 100 % ash recirculation which was not installed in Japan, and it became apparent that it was strongly related to the type of firing carried out.
The new catalyst was developed and tested in the pilot plants, resulting in the affirmation of its durability and its reliability for commercial use.
During the last 8 years we have increased the application of our SCR systems to various kinds of plants not only in Japan, but also Europe and the USA.
We are confident that if unexpected problems should occur in the future, our experiences and accumulated know how will enable us to correct any conceivable problems.

Operational experience

Having been awarded 30 plants for gas firing, 27 for oil firing, 28 for coal firing and 5 miscellaneous plants. Among these plants, in the field of utility operating are 10 plants for gas firing, 18 for oil firing and 19 for coal firing as of January 1989 (Others in this field are under design or construction).

Typical operational experience (utility) of SCR systems for three types of fuel gas, oil, and coal is summarized in Fig. 2.
It can be seen generally that the DeNOx catalyst deteriorates comparatively quickly during short periods from the start up, then stabilizes. Although the catalyst life is greatly dependent upon its operational conditions, the longest operation without catalyst replacement or addition among the above mentioned plants is about 9 years for gas firing, about 8 years for oil firing and about 6 years for coal firing.

Countermeasures to Deterioration of Catalyst

The deterioration of the catalyst due to aging is inevitable over a long period of time in the operation of a SCR system, therefore preventative countermeasures are an important subject. However the deterioration rate of the catalyst is relatively slow, and there are economical means to make most of the remaining catalyst activity.
The dependence of the volume of catalyst required with operating time is compared for the additional method and the replacement method in Fig. 3.
It is clear that the addition method is more advantageous, as it utilizes the remaining activity of the catalyst more effectively.

The plate type catalyst is particularly advantageous if the addition method is used, because additional catalyst units can be stacked directly on the initially loaded catalyst in the vertical gas flow arrangement (4).

The first commercial SCR system treating whole flue gas from the boiler was commissioned in 1978 at Chita No. 5 and No. 6 of Chube Electric Power Co. (respectively 700 MW gas firing).
They had operated for approx. 9 years without a catalyst addition or replacement. Then, the partial replacement followed.

Concerning SCR systems for coal fired boilers, the largest SCR plant for coal fired boilers in Japan was commissioned in 1983 at Takehara Power Station No. 3 of Electric Power Development Company (700 MW) and in 1986 at Duernrohr Power Station No. 1 and NO. 2 of VKG/EVN in Austria (405 MW and 352 MW respectively) went into commercial operation.

As for combined cycle/cogeneraton plants the first SCR plant was commissioned in 1981 at Kawasaki P.S. of Japanese Railway (141 MW). It operated for about 8 years without a replacement or addition of catalyst (3), (5).
Thereafter, a replacement was carried out and it has continued operating.

The first NOx removal system for a cogeneration plant in the USA was commissioned in early 1986 at Willammette Industries Inc. in California in the USA (8).
It has been operating satisfactorily for about 25,000 hours since its start up. We would like to introduce photographs with some specifications of the above mentioned plants.

- Fig. 4 : SCR plants at Chita No. 5 and No. 6 of Chubu E.P.Co.
  700 MW gas firing
  First plant treating whole gas exhausted from Japanese utility boilers
- Fig. 5 : SCR plant at Takehara No. 3 of Electric Power Development Company (EPDC) 700 MW coal firing
  The largest coal fired plant in Japan
- Fig. 6 : SCR plants at Duernrohr No. 1 and No. 2 of VKG/EVN
  405 MW and 352 MW coal firing
  First plants treating whole exhaust gas from boilers in Europe
- Fig. 7 : SCR plant at Kawasaki No. 1 of Japanese Railway 141 MW combined cycle plant
  First plant in the world treating exhaust gas from a combined cycle
- Fig. 8 : SCR plant at Willammette Industries Inc. in California
  22 MW cogeneration plant
  First plant treating exhaust gas from cogeneration plant in the USA

Next, the catalyst resistant to As which is newly developed is outlined.

Mechanism of Catalyst Poisoning by As

Since 1984, we conducted about 20 pilot tests in Europe as described before for the demonstration of the applicability of the catalyst developed by us. During these pilot tests, we found a certain decrease in activity of the catalyst in a few plants. After extensive investigations, it was finally discovered that the trace element Arsenic (As) in flue gas caused its deterioration.
Fig. 9 shows representative results, DeNOx efficiency and the concentration of As on the surface of the catalyst, obtained in our laboratory from the analyses of the sample catalysts taken out from the pilot plants after 6,000 - 9,000 hours operation. In this figure, DeNOx efficiency was measured under our standard test conditions.
It is apparent that in the case whereby the catalyst was used in the flue gas from the wet bottom boiler with 100 % ash recirculation, a considerable decrease in

activity of the catalyst occurs simultaneously with a rapid increase of As. The research work such as the analysis of elements adhered to the DeNOx catalyst was done to find the causes and mechanisms of the deterioration of the catalyst in our research laboratories.

Fig. 10 illustrates the general concept of catalyst poisoning by As which was obtained from the research. In the case whereby As is not contained in the flue gas, NH_3 is adsorbed on the active site of the catalyst and then reacts with NOx to form N_2 and H_2O. However, when As exists in the flue gas, it is adsorbed on the catalyst active site. Consequently, the adsorption of NH_3 is obstructed, resulting in the deactivation of the DeNOx catalyst.

Enrichment of As in the Boiler System

According to Ray et al's paper (6), the trace elements contained in coal are roughly classified into the following three groups depending upon their behavior as shown in Fig. 11.

- Group A : Concentration in bottom ash is almost the same as that in fly ash
- Group B : Selectively condensed on fly ash
- Group C : Emitted to stack as gaseous phase

Among the above three groups, the trace elements in Group B such as Ga, Cu, Pb, As etc. take upon a special behavior in the coal fired wet bottom boilers with ash recirculation.

Fig. 12 shows the comparison of the behavior of the trace element As "without ash recirculation" and "with ash recirculation". Because of the condensation effect of As, the total amount of As in the flue gas from the boiler with 100 % ash recirculation becomes about 8 to 11 times higher than that without ash recirculation. And according to Gutberlet (7), the gaseous concentration of As in the flue gas before an air preheater becomes several hundred $\mu g/Nm^3$ in the case of 100 % ash recirculation plants, although it is about 5 - 20 $\mu g/Nm^3$ for the wet bottom boilers without ash recirculation and less than 1 $\mu g/Nm^3$ for the dry bottom boilers. This condensation effect is closely related to catalyst deterioration by As described above.

Development of New Catalyst Resistant to As

Through careful investigations and painstaking studies it was found that the deterioration of the catalyst is caused by the accumulation of As on the catalyst and the development of New Catalyst resistant to As started to solve this problem. Some of the approaches for the solution were shown in Fig. 13.

Firstly we tried to reduce the pore-sizes of catalyst
When the As compound in flue gas is As_4O_6, its diameter would be approx. 7-8 Å, larger than that of NO and NH_3, approx. 3-4 Å. If the size of pore-diameter is controlled approx. 5-6 Å with technology of catalyst production, As compound is shut off from the pores, which will result in the prevention of deterioration by As.

Another approach was the investigation and study for the ingredients which have less adsorption ability of As.
As is adsorbed on the active site of NH_3 and obscures the NH_3 adsorption. If the affinity of active site with NH_3 is stronger than As, the catalyst activity will be able to be kept high.

Furthermore, we investigated the improvement of active site by the special treatment in order to protect the active site from As.

Several hundreds of catalysts were produced, and tested for the evaluation of resistance to As in the laboratory. Then the selected catalysts were installed in the pilot plants for the demonstration of their applicability. Finally, we came to the conclusion that the TiO_2 based catalyst in which the active site is improved by the special treatment is the most effective countermeasures.
Fig. 14 shows the test results of the New Catalysts developed for wet bottom which were taken out from the pilot plants in comparison with the ordinary catalysts for dry bottom. The results were satisfactory and the New Catalyst durability was ascertained.
The New Catalyst have already supplied to the commercial plants.

SUMMARY

1. For the last 8 years in the 1980s the application of our SCR systems has been expanded from dry bottom boilers to various kinds of plants such as wet bottom boilers, fluidized bed boilers, heat recovery steam generators, diesel engines, iron and steel plants etc., and not only in Japan, but also Europe and the USA.
2. In FRG we experienced a certain decrease in activity of the catalyst due to As adsorption in a few plants which were operated in slag tap boilers with 100 % ash recirculation.
3. The investigation and studies for a catalyst resistant to As were sucessfully performed and we developed a New Catalyst for Commercial utilization.

4. We are confident that if unexpected problems should occur in the future, our experiences and accumulated know how will enable us to correct any conceivable problems.

ACKNOWLEDGMENT

This paper contains data which were obtained in cooperation with the domestic or overseas electric power companies and with our lincensees of this process.
The authors wish to express their thanks to them.

REFERENCES

(1) H. Kuroda, F. Nakajima "Some Experience of NOx Removal in Pilots and Utility Boilers" EPRI FP-1109-SR Seminor proceedings, July 1979.

(2) T. Narita, H. Kuroda et al. "Babcock-Hitachi NOx Removal Process for Flue Gases form Coal-fired Boilers" IERL-RTP-1084
The EPRI/EPA joint Symposium on Stationary Combustion NOx Control Denver Colorado USA, Oct., 1980

(3) T. Narita, T. Kumura "DeNOx Equipment of Combined Cycle Power Plant" CIMAC 1983.

(4) H. Kuroda, T. Masai "Babcock Hitachi NOx Abatement Technology" NOx Symposium Karlsruhe, West Germany Feb., 1986.

(5) H. Kuroda, T. Ishikawa, T. Murataka "Latest DeNOx System for Combined Cycle Plant" CIMAC 1987.

(6) Ray, S.S. and Parker, F.G. : Characterization of Ash From Coal-Fired Power Plants. Springfield, VA : National Technical Inforamtion Services, January 1977.

(7) H. Gutberlet "Influence of Furnace Type on Poisoning of DeNOx Catalyst by Arsenic" VGB Kraftwerks Technik Vol. 68 No. 3 March 1988 (English Issue).

(8) M.G. Radin, B. Boyles "Turbine Exhaust Gas DeNOx Using Selective Catalytic Reduction" American Power Conference, April 1987.

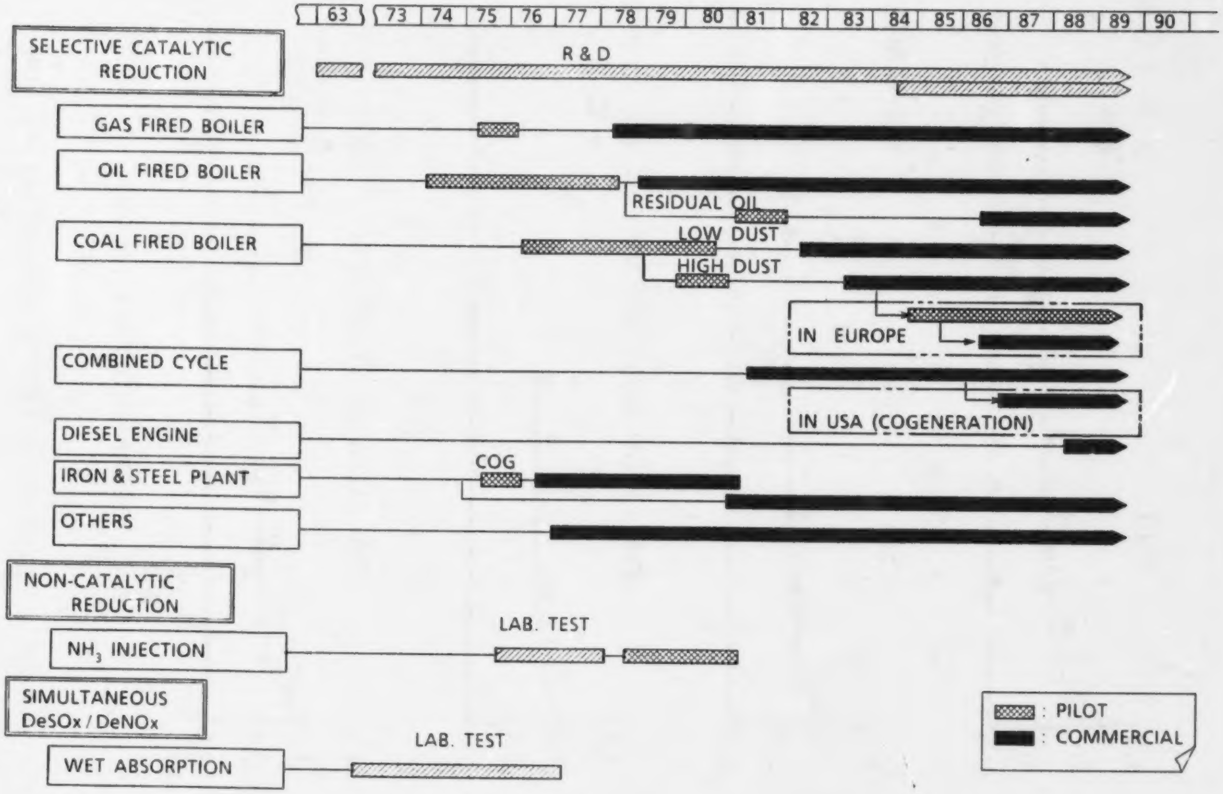


Fig. 1 DEVELOPMENT OF BABCOCK-HITACHI DeNOx PROCESS

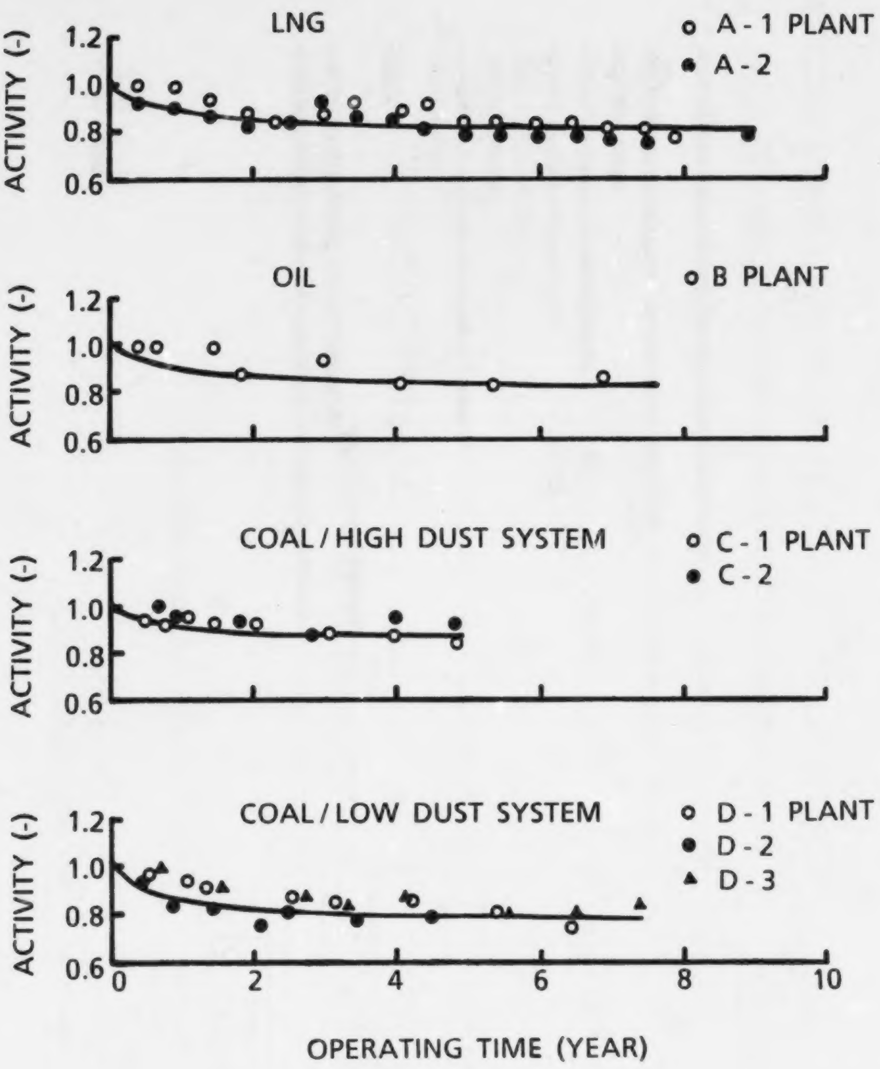


Fig. 2 CATALYST ACTIVITY WITH OPERATING TIME

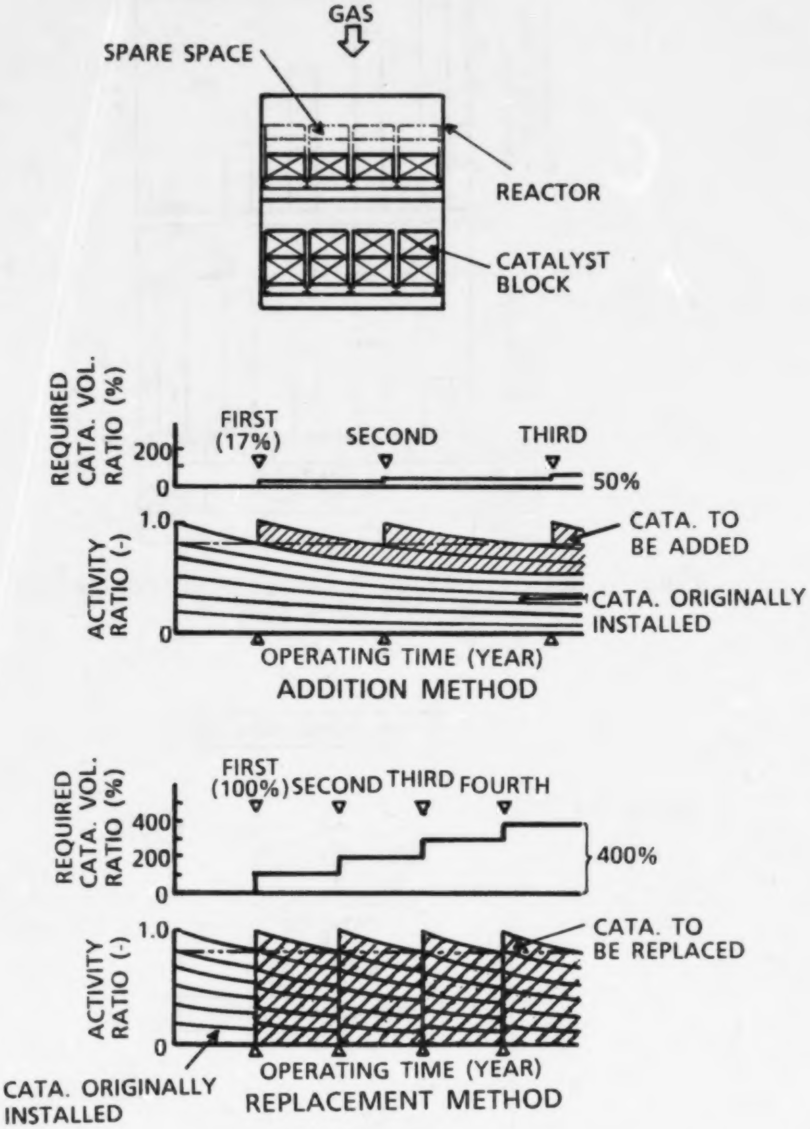


Fig. 3 COMPARISON OF THE ADDITION METHOD WITH THE REPLACEMENT METHOD

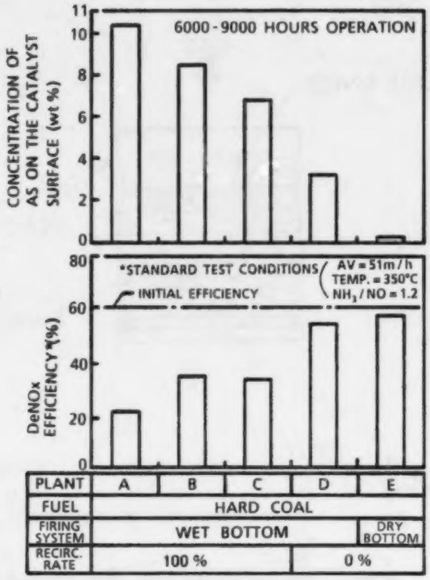


Fig. 9 RELATION BETWEEN CATALYST DETERIORATION AND TYPE OF BOILER

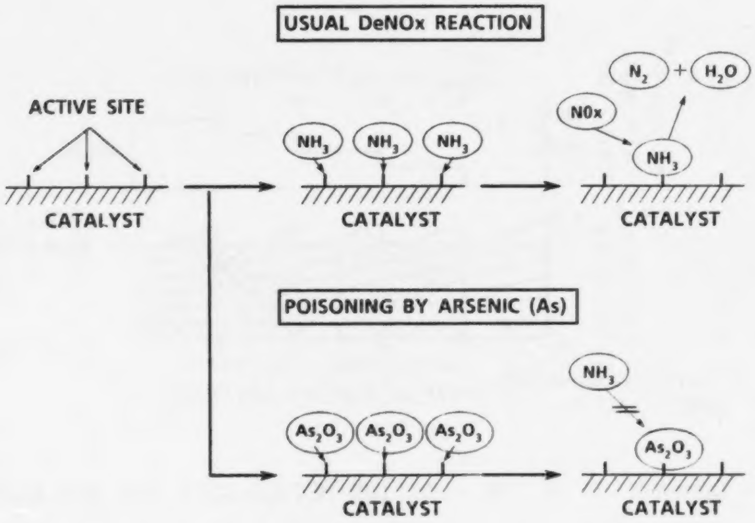
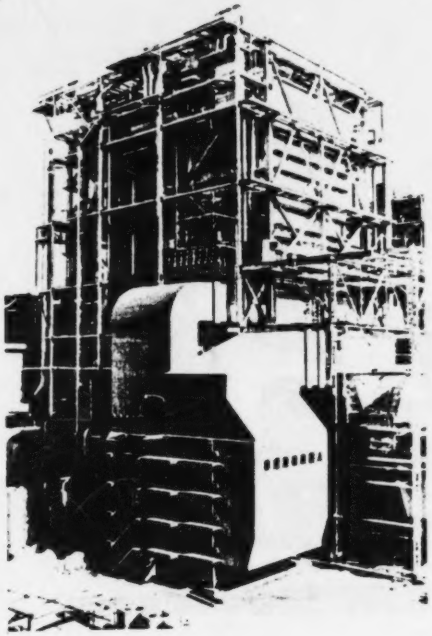


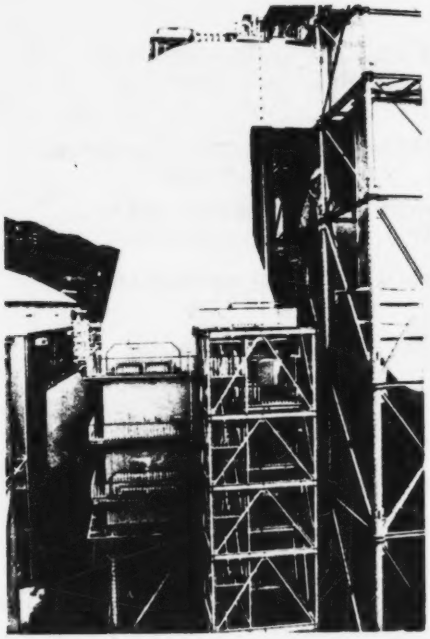
Fig. 10 MECHANISM OF CATALYST POISONING

Reproduced from
best available copy.



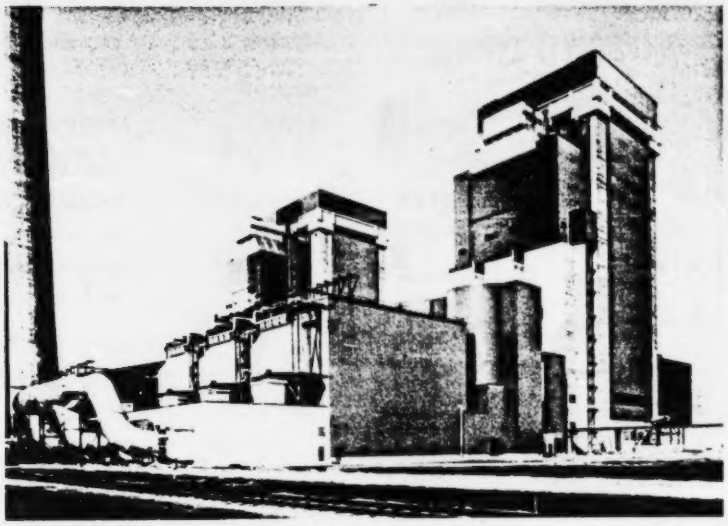
CUSTOMER : CHUBU ELECTRIC POWER CO.
CHITA P.S. No.5 & No,6 UNITS
BOILER FUEL : LNG
PROCESS : SELECTIVE CATALYTIC REDUCTION
GAS QUANTITY : 1,910,000 Nm3/h
(EQV. 700 MW)
INLET NOx CONC. : 50 ppm (5% O_2)
DeNOx EFF. : 80 % or MORE
OPERATION : MAR. 1978 (No.5)
MAY. 1978 (No.6)

Fig. 4 SCR PLANTS AT CHITA P.S. OF CHUBU E.P.CO.



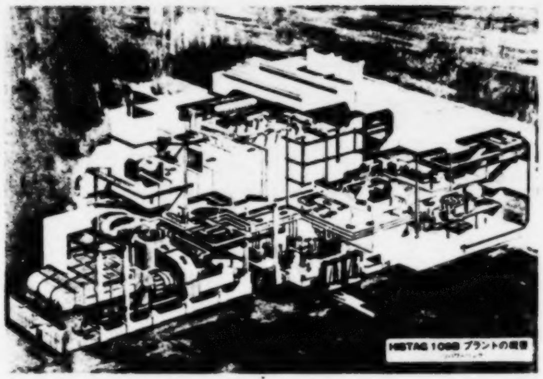
CUSTOMER : E.P.D.C.
: TAKEHARA P.S. NO.3 UNIT
BOILER FUEL : COAL
PROCESS : SELECTIVE CATALYTIC REDUCTION
GAS QUANTITY : 2,320,000 Nm3/h
(EQV. 700 MW)
INLET NOx CONC. : 300 ppm
DeNOx EFF. : 80 % or MORE
OPERATION : MAR. 1983

Fig. 5 SCR PLANT AT TAKEHARA P.S. OF E.P.D.C.



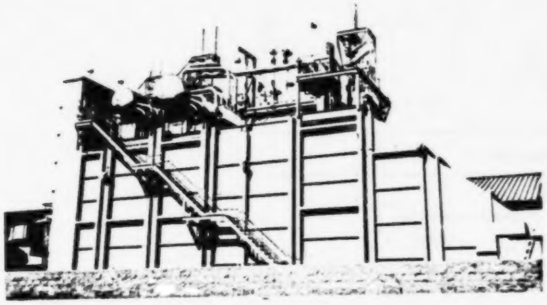
CUSTOMER	:	VKG DUERNROHR P.S. No.1 UNIT	EVN DUERNROHR P.S. No.2 UNIT
BOILER FUEL	:	COAL	COAL
PROCESS	:	SELECTIVE CATALYTIC REDUCTION	SELECTIVE CATALYTIC REDUCTION
GAS QUANTITY	:	1,210,000 Nm3/h (EQV. 405 MW)	1,038,000 Nm3/h (EQV. 352 MW)
INLET NOx CONC.	:	800 mg/Nm3 (6% O_2) (390 PPM)	650 mg/Nm3 (6% O_2) (317 PPM)
DeNOx EFF.	:	80 % or MORE	80 % or MORE
OPERATION	:	MAR. 1987	MAR. 1987

Fig. 6 SCR PLANTS AT DUERNROHR P.S. OF VKG & EVN



CUSTOMER : JAPANESE RAILWAY
: KAWASAKI P.S. No.1 UNIT
FUEL : KEROSENE
PROCESS : SELECTIVE CATALYTIC REDUCTION
GAS QUANTITY : 1,024,000 Nm3/h
(EQV. 141 MW ; MS9001B)
DeNOx EFF. : 80 % or MORE
OPERATION : FEB. 1981

Fig. 7 SCR PLANT AT KAWASAKI P.S. OF JAPANESE RAILWAY



CUSTOMER : WILLAMETTE INDUSTRIES, INC
FUEL : NATURAL GAS
PROCESS : SELECTIVE CATALYTIC REDUCTION
GAS QUANTITY : 195,000 Nm3/h
(EQV. 22 MW ; GE LM5000)
INLET NOx CONC. : 75 ppm (15% O_2)
DeNOx EFF. : 80 % or MORE
OPERATION : MAY. 1986

Fig. 8 SCR PLANT AT WILLAMETTE INDUSTRIES INC.

GROUP A
CONCENTRATION IN BOTTOM ASH = CONCENTRATION IN FLY ASH
Al Ce Fe La Rb Sm Th Ba Co Hf Mg Sc Sr Ti Ca Eu K Mn Si Ta

GROUP B
SELECTIVELY CONDENSED ON FLY ASH
As Ga Sb Cd Mo SE Cu Pb Zn

GROUP C
EMITTED TO STACK AS GASEOUS PHASE
Hg Cl Br

Fig. 11 BEHAVIOR OF THE TRACE ELEMENTS IN COAL

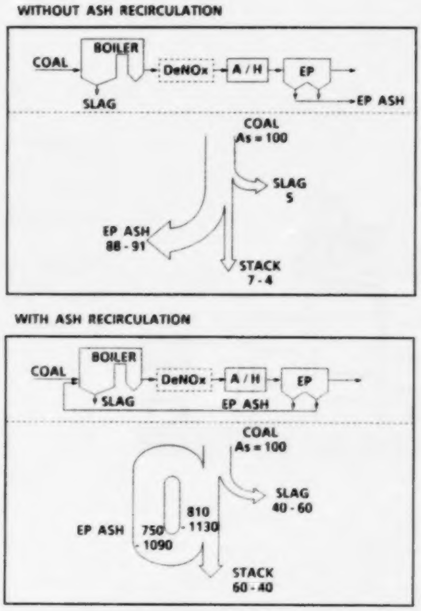


Fig. 12 ENRICHMENT OF ARSENIC (As)

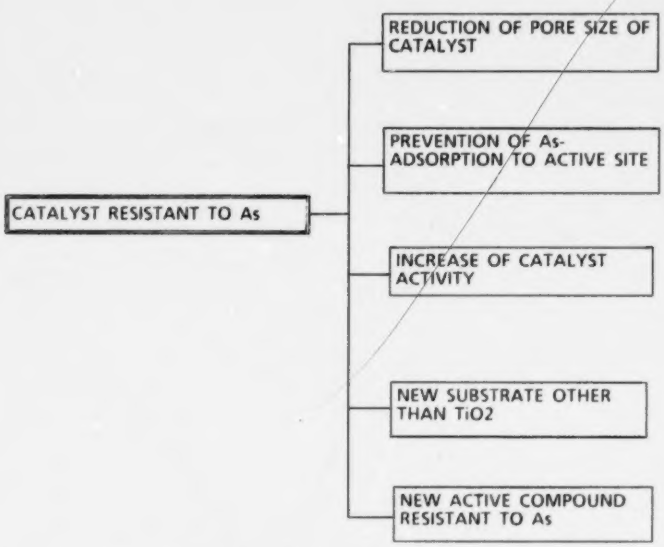

CATALYST RESISTANT TO As
REDUCTION OF PORE SIZE OF CATALYST
PREVENTION OF As-ADSORPTION TO ACTIVE SITE
INCREASE OF CATALYST ACTIVITY
NEW SUBSTRATE OTHER THAN TiO2
NEW ACTIVE COMPOUND RESISTANT TO As

Fig. 13 APPROACHES FOR THE DEVELOPMENT OF CATALYST RESISTANT TO As

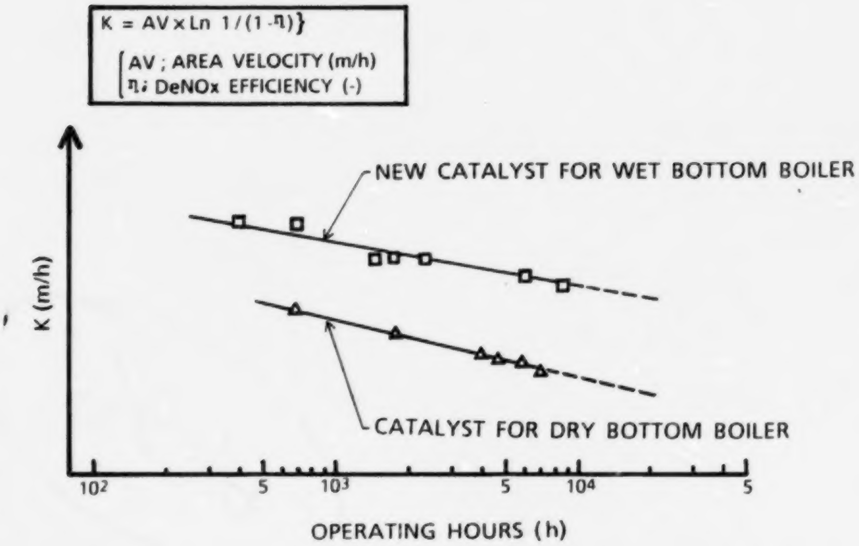


Fig. 14 OPERATING HOURS VS K IN WET BOTTOM BOILER (EXAMPLE)

THE FIRST DE-NOx INSTALLATION IN THE NETHERLANDS
A DEMONSTRATION PROJECT AT EPON - NIJMEGEN POWER STATION

Ir. J.M. Koppius-Odink
N.V. EPON
8025 AZ ZWOLLE
The Netherlands

Ir. W.L.C. Weier
N.V. KEMA
6812 AR ARNHEM
The Netherlands

Dr. Ir. W.L. Prins
ESTS BV
1970 AL VELSEN-NOORD
The Netherlands

ABSTRACT

In order to demonstrate the feasibility of the Japanese SCR technology in 1985 a demonstration installation has been installed by ESTS BV for denitrification of the fluegases from the coal fired boiler No. 12 at EPON, Centrale Gelderland, Nijmegen. The DeNox plant handles 50% of the fluegases. This national demo project is financed by the Government through the N.V. NOVEM. Initial start-up was in 1987.

From this demo project experience is reported on:

- Operating performance of the installation, performance of the individual catalyst layers, experience on catalyst consumption and inspection results.
- Consequences of ammonia slip: experience with possible fouling of air preheater, E-filter, ducts and fan. Determining the effect of residual NH_3 in the flyash application.
- Operating experience with:
  - NH_3 injection: control quality, distribution of NH_3 injection over the catalyst, fouling of ammonia-injection nozzles;
  - a specially developed by-pass gas mixer;
  - plant instrumentation for monitoring NH_3, NO_x and SO_3;
  - soot blowing;
  - maintenance.

At the end of this demonstration project (1989) an economic evaluation based on this experience will be made.

Preceding page blank

INTRODUCTION

EPON installed at the location Nijmegen (The Netherlands) a demonstration installation for denitrification of the flue gases from the coal fired boiler No. 12. This project was financed by the Government, through the Netherlands Agency for Energy and the Environment (NOVEM), in a joint effort by the The Ministry of Environmental Affairs and The Ministry of Economic Affairs.
The purpose of this national demo project is to demonstrate the feasibility of the Japanese SCR technology in the Netherlands. The plant has been constructed by ESTS BV in 1986. KEMA, the joint organisation of the Dutch Utilities, is primarily involved in the execution of the measurements. In the future this project will give a contribution to a practical construction, operation and exploitation of this kind of technology in the Netherlands.

After explanation of the targets of the project and a description of the denox system, experience will be reported going step by step through the denox installation:
- eco bypass, temperature control
- (bypass) fluegas mixer
- ammonia supply, injection and mixing
- reactor and catalyst
- soot blowing
- flyash transport system
- down stream equipment: air preheater, E.S.P. and I.D. Fan
- fly ash application
- control system and monitoring equipment
- maintenance
- conclusions

THE DEMO PROJECT

Relevant items for demonstration in this project are:

- Operating performance of the installation, performance of the individual catalyst layers, experience on catalyst consumption and inspection results.

- Consequences of ammonia slip: experience with possible fouling of air preheater, E-filter, ducts and fan. Determining the effect of residual NH_3 in the fly ash application.

- Operating experience with:
    - NH_3 injection: control quality, distribution of NH_3 injection over the catalyst cross-section, fouling of ammonia-injection nozzles;
    - a specially developed by-pass gas mixer;
    - plant instrumentation for monitoring NH_3, NO_x and SO_3;
    - soot blowing;
    - maintenance.

At the end of this demonstration project (1989) an economic evaluation based on this experience will be made.

THE DENOX INSTALLATION

The retrofit denox installation is of the high dust, high temperature, type.

The main data for the Electricity Generation Unit are:

Utility : EPON, Zwolle
Unit : Gelderland, Unit 12, in operation since 1966
Location : Nijmegen, The Netherlands
MW el : 125 MW
Type of boiler : U-firing
Fuel type : imported bituminous coal (heavy fuel oil)

The data for the SCR plant are:

Fluegas flow : 210.000 m_o^3/h (50% of the total fluegas flow)
Operating fluegas temperature : 320-400°C (Eco outlet)
NOx content (inlet) : 509 ppm vol. at 3% O_2
Removal efficiency : > 80%
NH_3 slip : < 5 ppm
Load variation : 40 - 100%
Catalyst type : Honeycomb
Catalyst manufacturer: MHI
Number of catalyst layers : 3
Dummy layer : 1
Total volume catalyst: 95 m^3
L x B x H of reactor : 9,1 x 5,1 x 25 m
Guarantee period : 2 years

In the design of the system a special problem was the little place available for the reactor. The space between the E.S.P's has been utilised.
Only one of the two fluegas streams (50%) is treated by the denox installation. This makes it possible to compare flyash from the denox plant and similar flyash from the stream without denox. A separate flyash silo for the denox flyash was installed. In this way both flyash sorts can be tested for applications.
In order to compensate the additional pressure drop from the reactor a new induced draft fan has been installed.
Figure 1 gives an overview on the installation. Figure 2 gives a scheme of the system.
After the economiser the fluegas stream is split into two ducts leading to the two air preheaters. In one of the two ducts the SCR reactor is installed. A bypass over the economiser is installed with a fluegas flow control valve. In this way the fluegas temperature in the reactor can be controlled. The eco-bypassed fluegases are mixed in a specially, for this purpose developed, mixer.

ECONOMISER BYPASS; TEMPERATURE CONTROL OF INLET FLUEGAS

After start-up in December 1986 it appeared that the inlet temperature was too low to allow the Denox-reactor to operate with ammonia injection. To prevent ammoniumbisulfate formation in the catalyst the minimum continuous inlet temperature at design SO_3 level should be 340°C. Only short operation between 320-340°C is allowed if it can be followed by "regeneration" by controlling the inlet

Even with open bypass, measurements showed that the inlet temperature could not be raised sufficiently. Therefore early 1987 the economiser was modified, with the result that inlet temperatures were obtained as described above.
In practice the eco-bypass is operated now always completely open. At partial load (below 80%) however, the inlet temperature is still too low (below 320°C). Ammonia injection is stopped in that situation.

THE BYPASS FLUEGAS MIXER

In order to get an uniform temperature distribution at the inlet of the reactor and specially since lower temperatures are not allowed in the catalyst, a fluegas mixer was installed to mix the appr. 450°C Eco-bypass flow with the 300°C Eco-outlet flow. A specially for this application developed fluegas mixer (see fig. 3) is installed.
The velocities of different adjacent layers of fluegases are approx. 22 m/s. and 5 m/s. and are optimal for Eddy diffusivity with large turbulence. Good mixing (i.e. rel. standard dev. ≤10%) is obtained after 3 x diameter of the duct.
Advantages of this mixer are:

1. Fluegas at high velocity is not deviated in velocity direction; the low velocity fluegas is led around a bend.
2. The high velocity gas "pulls" the low velocity, gas saving fan capacity.

The system is free from flyash accumulation.

AMMONIA SUPPLY, INJECTION AND MIXING

One NH_3 storage tank is installed for this demo project, including an evaporator vessel and buffer vessel at the beginning of the NH_3 (vapour) transmission pipe of approx. 300 m. This system needed only minor attention like seal replacement and control valve cleaning.

The ammonia injection system is shown in figure 4. The distribution system has valves that can be used to influence the distribution in the fluegas. In case of fluegas velocity gradient in the duct ammonia injection should be adjusted to get homogenous concentrations of NH_3 in the fluegas. Already very good distribution was obtained with all valves in open position.
The injection is done by means of 16 injection pipes, each having 16 nozzles. During 11.000 operating hours only one pipe had to be cleaned.

In the fluegas duct ahead of the reactor a static mixer is installed to uniformly diffuse NH_3 through the fluegas. The static mixer consists of a grid of vertical pipes (for horizontal mixing) and horizontal pipes (for vertical mixing).

REACTOR AND CATALYST

The vertical flow reactor is formed by three catalyst layers, a dummy layer on top and soot blowers cleaning the top side of the catalyst layers.

Important characteristics for the reactor operation are:
- homogeneous temperature distribution and NH_3 concentration
- homogeneous gas velocity
- catalyst activity

TEMPERATURE AND NH_3 CONCENTRATION DISTRIBUTIONS

Homogeneous temperature and NH_3-concentration distributions at the inlet of the reactor are very important. Even with the precautions taken the temperature distribution at the inlet of the reactor was just acceptable. At the boiler side we found the lower temperatures, approx. 30°C below the average temperature. This underlines the necessity to give much attention to the mixing of the bypass flue gas stream with the main stream.
So far we could not obtain sufficient reliable values of the NH_3-concentration. In the meantime the measurement procedures are improved and we expect to get an impression of the NH_3-concentration distribution at the inlet shortly.

GAS VELOCITY DISTRIBUTION

After start up of the boiler during inspections severe flyash build up was established on the dummy layer at the boiler side, the inside of the corner of the reactor inlet. See figure 5. In figure 6 fluegas flow simulation result is given. It confirmes the observations of flyash build-up. Also the flow pattern was confirmed visually on the walls of the reactor. See figure 7.

From figure 6 also the effect of the dummy layer can be seen. The first layer of catalyst obtains a homogeneous gasflow by the operation of the dummy layer. Main purpose of the dummy layer is to direct the velocity of the flyash vertically. In future installations guide vanes should be considered above the dummy layer in an attempt to minimise the flyash build-up. In this installation static soot blowers were installed above the dummy layer on the locations with flyash build-up. They operate once a shift. As a result the flyash build up was decreased to acceptable levels for catalyst operation.

CATALYST LAYERS, ACTIVITY

During 11.000 hours boiler operation almost no flyash build-up was observed on top of the catalyst layers. Internal plugging of the honeycomb "channels" is only slowly progressing and is now in total a few percent of the catalyst area.

The denox removal efficiency of the catalyst layers is of course mainly determined by the molar ratio NH_3/NO_x at the inlet of the reactor. As is shown in figure 8-14 easily a NO_x removal efficiencies was obtained of 85% with the catalyst at start up. Long term operation at removal efficiencies far above 80% removal is not allowed.
Potential concentration gradients of NO_x and NH_3, or gas velocity gradients may cause NH_3 slip through the reactor, which leads to fouling of catalyst and downstream equipment by ammonium bisulfate.

The space velocity at design flow in the reactor is 2225 h^{-1}. The performance after 2500 operating hours of the individual layers can be seen from figures 8-11. The performance after 4500 hours is given in the figures 12-14.
From the figures can be seen that before the catalyst the NO_x and NO distribution is within the accuracy of the measurement method and the stability of the operating parameters in the reactor.
After the first catalyst layer the concentrations of NO_x equals the NO-concentration of meaning that all NO_2 is converted after one layer.
The conversion of NO_x is almost complete after the first layer. The concentrations

It is planned to take 3 catalyst samples each year and to test these samples accurately for activity in a bench-scale unit to "overcome" the inaccuracies in the measurements in the denox-plant.
The total denox-efficiency was approx. 75% during these measurements, since the control signal for NH_3-supply from the NO_x monitor at the inlet gave temporarily a lower molar ratio NH_3/NO_x.
After the three catalyst layers there is a profile in NO_x concentration (maximum concentration deviation is approx. 34-74% from the average).

AMMONIA SLIP

At the startup of the denox installation a low ammonia slip (smaller than 2 ppm) was determined. Also on this item measurements after the start-up had such an inaccuracy that until now no significant increase could be established.

SOOT BLOWING

Soot blowing of the catalyst layers appeared to be necessary in this installation. The frequency is once per day. This can perhaps be reduced. Because of the flyash build up on the dummy layer, this installation is not representative for soot blowing in future installations. It may be that in future installations the frequency of soot blowing can be reduced considerably.
The pressure drop over the reactor was maintained stable as shown in table 2.

FLYASH TRANSPORT SYSTEM

There were no special problems. Some wear of pipes for pneumatic transport occured.

DOWNSTREAM EQUIPMENT: AIR PREHEATER, E.S.P. AND I.D. FAN

AIR PREHEATER

Initially some very small white spots of a few mm's on the renewed lamella packages were observed. But no increase in amount was established in later inspections.

ELECTROSTATIC PRECIPITATOR

Until now visual inspection gave no difference in fouling behaviour in the EP's. In both cases the electrodes and plates were covered by a homogeneous layer of approx. 2 mm thickness.

I.D. FAN

On the blades no deposits were observed. However, on the axis some deposits were observed resulting in increase in unbalance. Installation of a soot blower solved this problem.

FLYASH APPLICATION

In the Netherlands flyash is used for several applications. If flyash is contaminated with ammonia, it could lead to problems when used for light-weight aggregate production, for fabrication of building stones and for production of concrete.

See for a detailed analysis for the coal and flyash table 3. There is no significant increase in NH_3 content in the flyash from the Denox system compared to the flyash from the fluegas without denox system. The relative short operating period does not allow conclusions on this item (the catalyst did not drop measurable in activity).
Tests planned to check the denox flyash in its application has therefore not yet been carried out; first a measurable increase in NH_4^+ in flyash has to be established.
In case the ammonia slip remains at this low levels, a test is considered by temporary increase of the NH_3/NO_x molar ratio to artificially establish an ammonia slip of a few ppm (design is < 5 ppm) and then collect flyash for analysis and possible testing in its applications.

THE CONTROL SYSTEM; MONITORING EQUIPMENT

BOILER CONTROL SYSTEM

At installation of the new induct draft fan with its higher operating pressure head and different characteristic a new fan control system had to be incorporated into the existing boiler control system.
Two turbine type fluegas flow meters were installed (see figure) at symmetrical positions in the gasstream in the high dust environment. The original control signal (boiler pressure) is going directly to the existing inlet vane control motor and via an arithmic function (a "curve) to the new inlet vane control motor.

The experience with this additional control system is that it was relative sensitive. Specially when the boiler did go up in load after a stop the system needed attention for complete stability. It must always be assured that the instrument air supply to the insertion turbine meter bearings is on.

The turbine meters function well; only an electronic's failure has been experienced until now.

NOx REMOVAL CONTROL SYSTEM

The fluegas flow signal shown in figure 15 forms together with the inlet NO_x concentration signal and the NH_3/NO_x molar ratio set at 0,8 the signal to the NH_3 feed control loop.

The outlet NO_x concentration signal is (together with the inlet NO_x signal) used to derive a signal for NO_x removal efficiency. This gives a correction to the signal to the NH_3 feed control loop in order to keep a constant NO_x-removal efficiency of 80%.
Boiler load fluctuations and fluctuations of inlet NO_x concentrations are accounted for by this control loop, keeping the NO_x removal at the required

Due to problems with the NO monitoring equipment (see below) an operation of this control loop has not been possible during a major part of the operating period. The NH_3 flow control loop was operated manually. In this situation the dynamic's of the control system could not be tested so far.

MONITORING EQUIPMENT

The analytical equipment is sampling in a high dust environment causing complications.

NO equipment :	In the infrared cells optics were fouled by As and Se, together with flyash. Thus As and Se are bound to fine flyash, therefore in the NO monitors after EP's this forms no problem. In the sampling line an EP and special filter have been installed, improving the reliability of the system. Still a systematic difference of 16-20°% with another method is existing. It is being investigated.
SO_3 equipment :	The installed equipment is not suitable for continuous measurement. Calibration is very time consuming. After calibration the equipment is reliable for only a few hours.
NH_3 equipment :	The equipment (range 0-10 ppm NH_3) is with the present catalyst activity operating near its detection limit. Laboratory methods applied however, give not yet consistent results.

MAINTENANCE

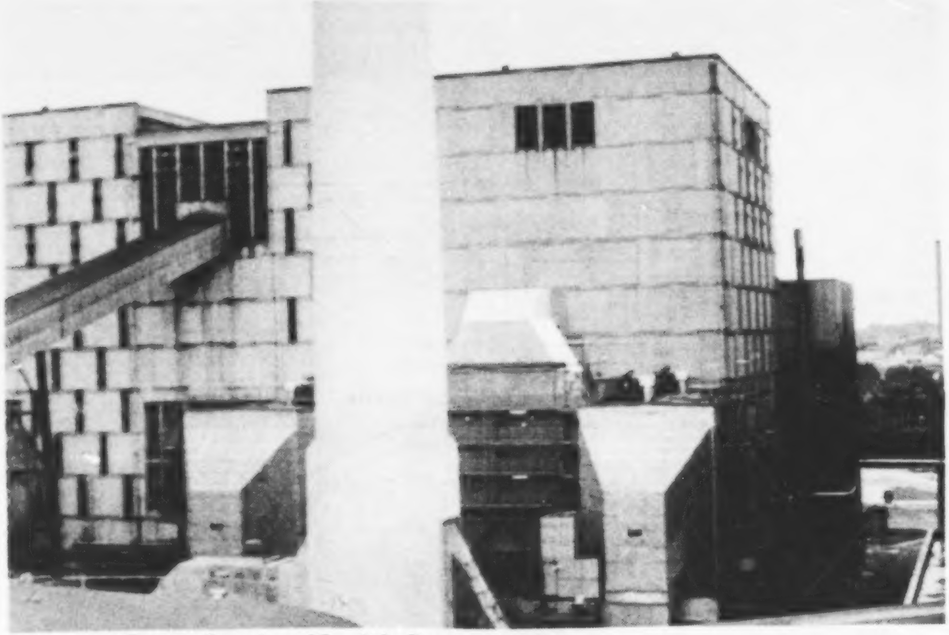
In figure 16 the maintenance hours by the electric/control department and the mechanical department are shown per section of the Denox plant.

CONCLUSIONS

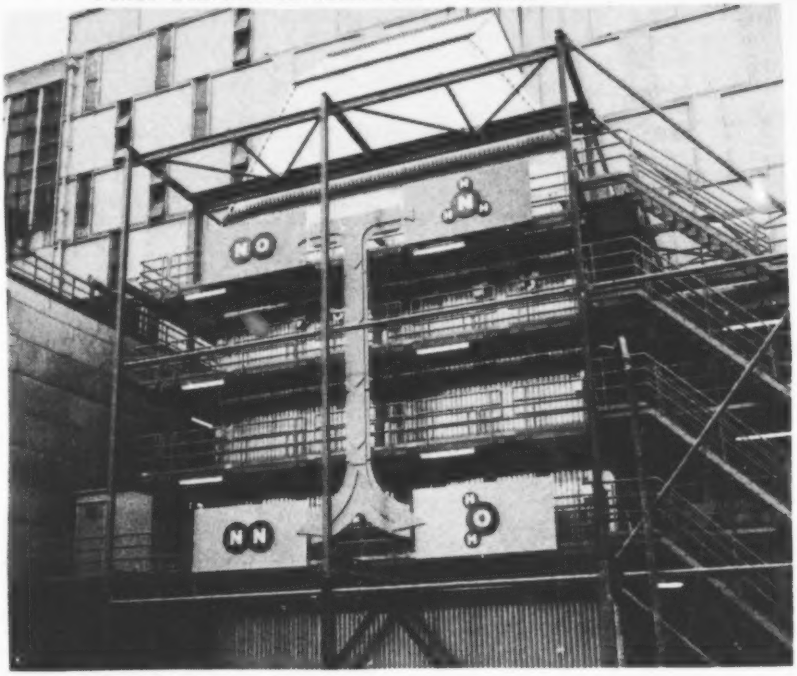
The main conslusions in this first part of the demo project are:

- The Denox system is operating well; catalyst activity reduction could not yet be measured after 4500 hours.
- Only minor fouling was observed in the downstream equipment after the Denox reactor.
- For new Denox-systems in the design fase data on operating temperatures after economiser and required inlet temperatures have to be checked carefully. This implies in particular for retrofit situations.
- Special attention in future systems for fluegas flow distribution at inlet of reactor is necessary. Guide vanes are in most cases necessary.
- Monitoring equipment (e.g. for NO_x) for future systems needs much attention to give sufficient reliable results. Maintenance attention is high.

Reproduced from
best available copy.



Power Station 12 with Denox reactor



Detailed view on reactor

Figure 1

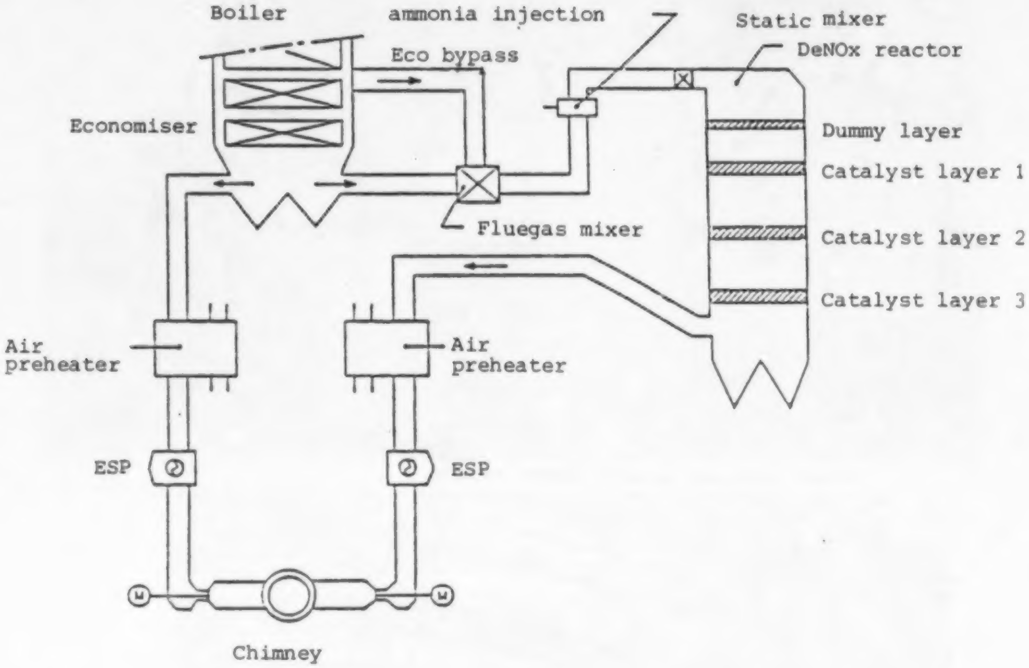


Figure 2. Scheme of the Denox Installation

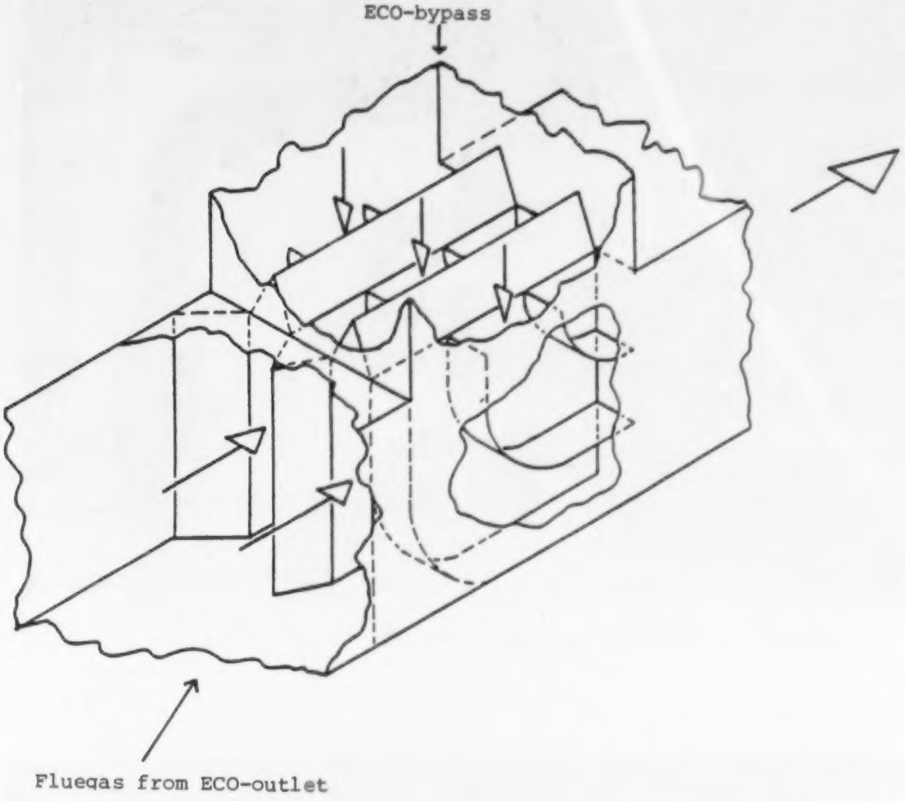


Figure 3. Schematic drawing of fluegas mixer

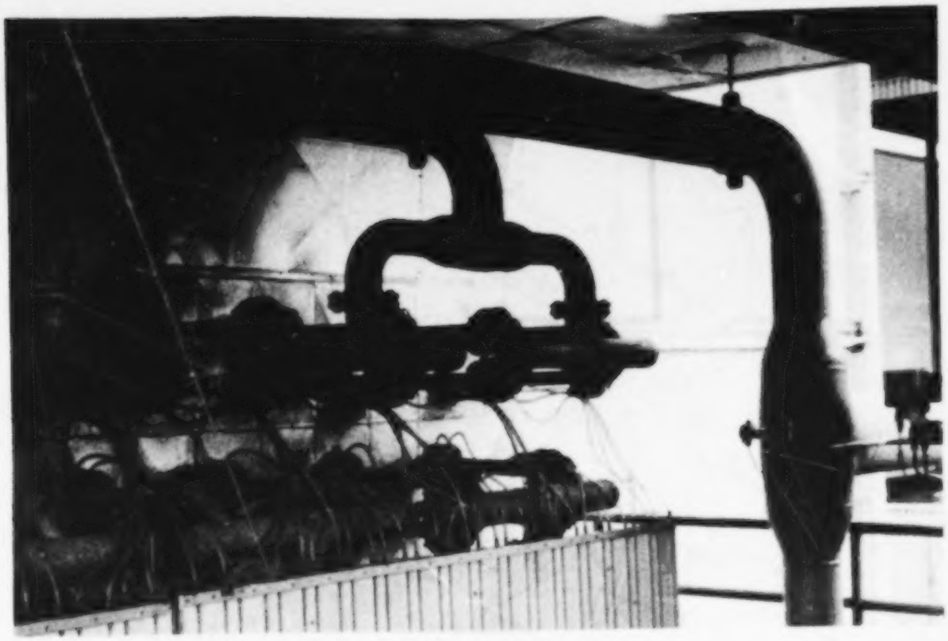


Figure 4. Ammonia injection system.

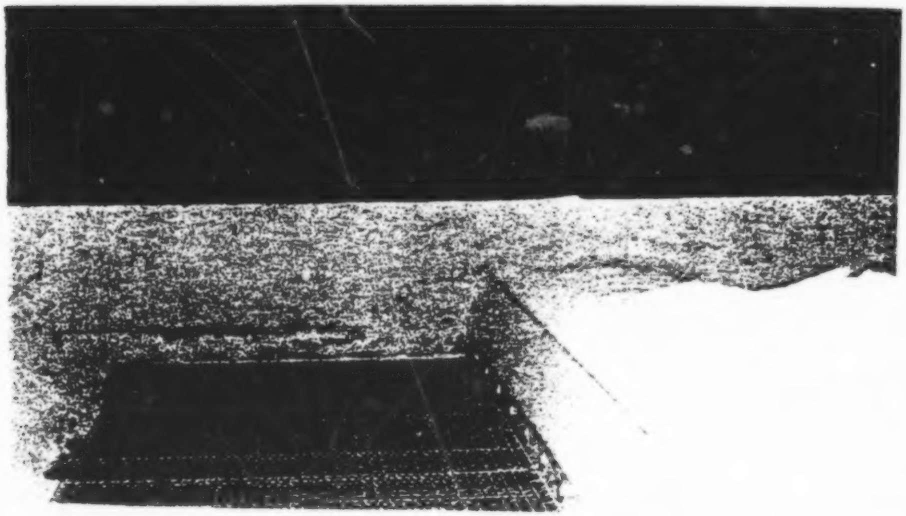


Figure 5. Flyash build up on dummy layer before soot blowing

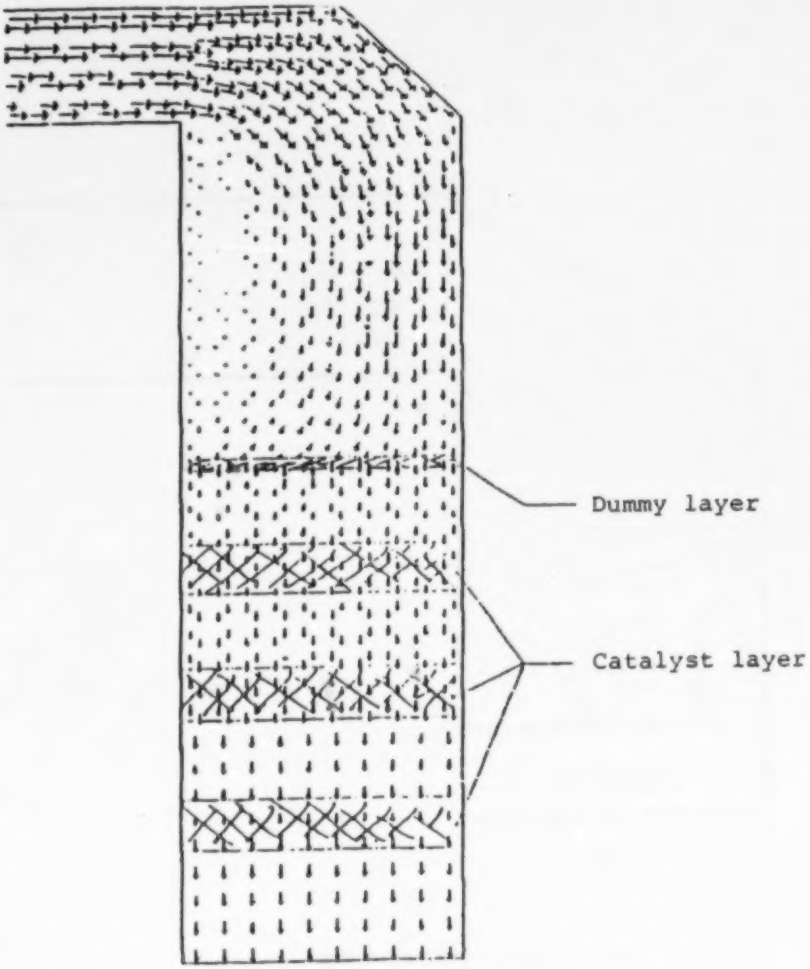


Figure 6. Calculated gasflow distribution.

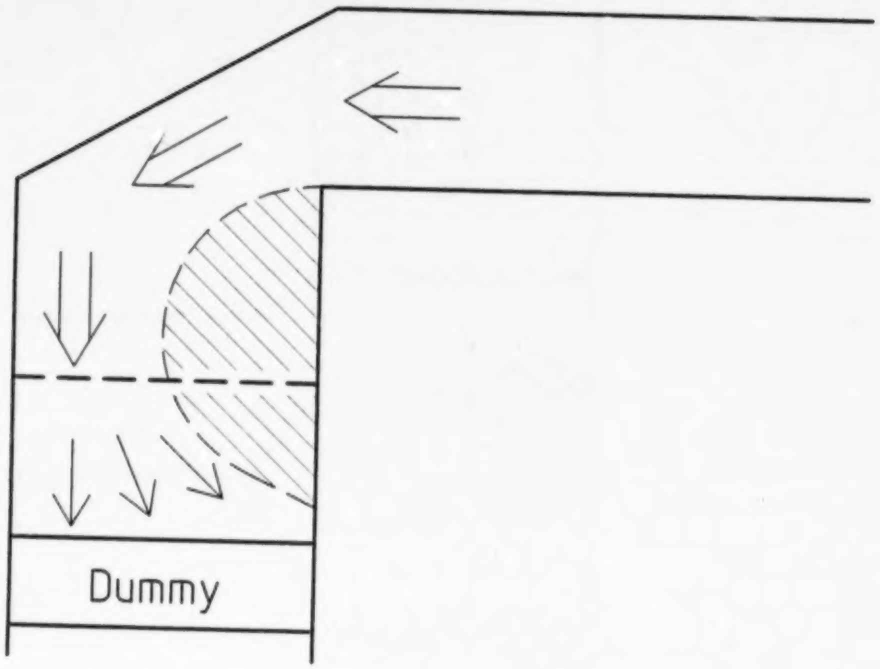


Figure 7. Gas velocity distribution

BOILERSIDE

distance in mm	7	6	5	4	3	2	1 nozzle No.
↓ 640	729 698 4,3		729 698 4,4		729 698 4,2	750 729 4,0	
1930	719 698 4,0		719 698 4,6		729 698 4,3	770 739 3,8	
1930	729 709 4,0		739 719 4,4		739 709 4,4	760 739 3,8	
640 ↑	739 719 4,3		739 719 4,4		750 719 4,3	750 729 4,0	

NO_x
NO } concentrations in mg/m^3_o
O_2

SUMMARY			
	NO_x	NO	O_2
	mg/m^3_o	mg/m^3_o	%
min.	719	698	3,8
av.	739	714	4,2
max.	770	739	4,6
Δ	51	41	0,8

Figure 8. No_x, NO and O_2 concentrations before 1st catalyst layer.

BOILERSIDE

distance in mm	7	6	5	4	3	2	1 nozzle No.
↓ 640	191 191 3,0		150 150 3,0		191 191 2,8		158 158 3,2
1930	201 201 2,9		168 168 3,5		195 195 3,0		158 158 3,1
1930	144 144 2,7		160 160 3,6		181 181 3,0		158 158 2,8
640 ↑	144 144 3,1		160 160 3,1		168 168 2,8		160 160 2,6

NO_x
NO } concentrations in mg/m^3_o
O_2

SUMMARY			
	NO_x	NO	O_2
	mg/m^3_o	mg/m^3_o	%
min.	144	144	2,6
av.	168	168	3,0
max.	201	201	3,6
Δ	57	57	1,0

Figure 9. No_x, NO and O_2 concentrations between 1st and 2nd catalyst layer.

BOILERSIDE

distance in mm	7	6	5	4	3	2	1 nozzle No.
↓ 640	154 154 3,4		109 109 3,5		103 103 3,6		160 160 3,6
1930	160 160 3,4		94 94 3,7		92 92 3,7		129 129 3,6
1930	150 150 3,7		78 78 3,6		76 76 3,7		123 123 3,6
640 ↑	123 123 3,5		78 78 3,4		76 76 3,5		117 117 3,5

NO_x
NO } concentrations in mg/m^3_o
O_2

SUMMARY			
	NO_x	NO	O_2
	mg/m^3_o	mg/m^3_o	%
min.	76	76	3,4
av.	114	114	3,6
max.	160	160	3,7
Δ	84	84	0,3

Figure 10. No_x, NO and O_2 concentrations between 2nd and 3rd catalyst layer.

BOILERSIDE

nozzle No.				
↓ 7	236 236 4,8	201 201 5,0	175 175 4,8	226 226 4,6
6				
5				
4				
3	226 226 5,2	181 181 5,1	164 164 4,9	195 195 5,0
2				
1 ↑	212 212 5,0	189 189 5,0	170 170 4,8	201 201 4,8
	640	1930	1930	640

NO_x
NO } concentrations in mg/m_o^3
O_2

SUMMARY			
	NO_x	NO	O_2
	mg/m_o^3	mg/m_o^3	%
min.	164	164	4,6
av.	198	198	4,9
max.	236	236	5,2
Δ	72	72	0,6

Figure 11. No_x, NO and O_2 concentrations downstream 3rd catalyst layer.

BOILERSIDE

distance in mm	7	6	5	4	3	2	1 nozzle No.
↓ 640		631 589 4,8		633 592 5,1		645 604 5,3	
1930		631 589 4,9		645 604 5,2		663 622 5,3	
1930		645 604 4,9		657 616 4,6		653 612 4,5	
640 ↑		645 604 5,0		657 616 4,4		651 610 4,6	

NO_x
NO } concentrations in mg/m_o^3
O_2

SUMMARY			
	NO_x	NO	O_2
	mg/m_o^3	mg/m_o^3	%
min.	631	589	4,4
av.	646	605	4,9
max.	663	622	5,3
Δ	32	33	0,9

Figure 12. No_x, NO and O_2 concentrations before 1st catalyst layer.

BOILERSIDE

distance in mm	7	6	5	4	3	2	1 nozzle No.
↓ 640		210 210 5,4		187 187 5,4		154 154 5,1	
1930		210 210 5,4		177 177 5,6		144 144 5,0	
1930		195 195 5,5		164 164 5,2		144 144 5,0	
640 ↑		203 203 5,4		191 191 5,2		156 156 5,0	

NO_x
NO } concentrations in mg/m_o^3
O_2

SUMMARY			
	NO_x	NO	O_2
	mg/m_o^3	mg/m_o^3	%
min.	144	144	5,0
av.	178	178	5,3
max.	210	210	5,6
Δ	66	66	0,6

Figure 13. No_x, NO and O_2 concentrations between 1st and 2nd catalyst layer.

BOILERSIDE

distance in mm	7	6	5	4	3	2	1 nozzle No.
↓ 640		183 183 5,0		144 144 5,3		138 138 4,8	
1930		173 173 5,2		142 142 5,4		107 107 5,1	
1930		152 148 5,0		121 121 4,8		84 84 4,5	
640 ↑		148 148 5,5		115 115 4,8		82 82 4,6	

NO_x
NO } concentrations in mg/m^3_o
O_2

SUMMARY			
	NO_x	NO	O_2
	mg/m^3_o	mg/m^3_o	%
min.	82	82	4,5
av.	132	132	5,0
max.	183	183	5,5
Δ	101	101	1,0

Figure 14. No_x, NO and O_2 concentrations between 2nd and 3rd catalyst layer.

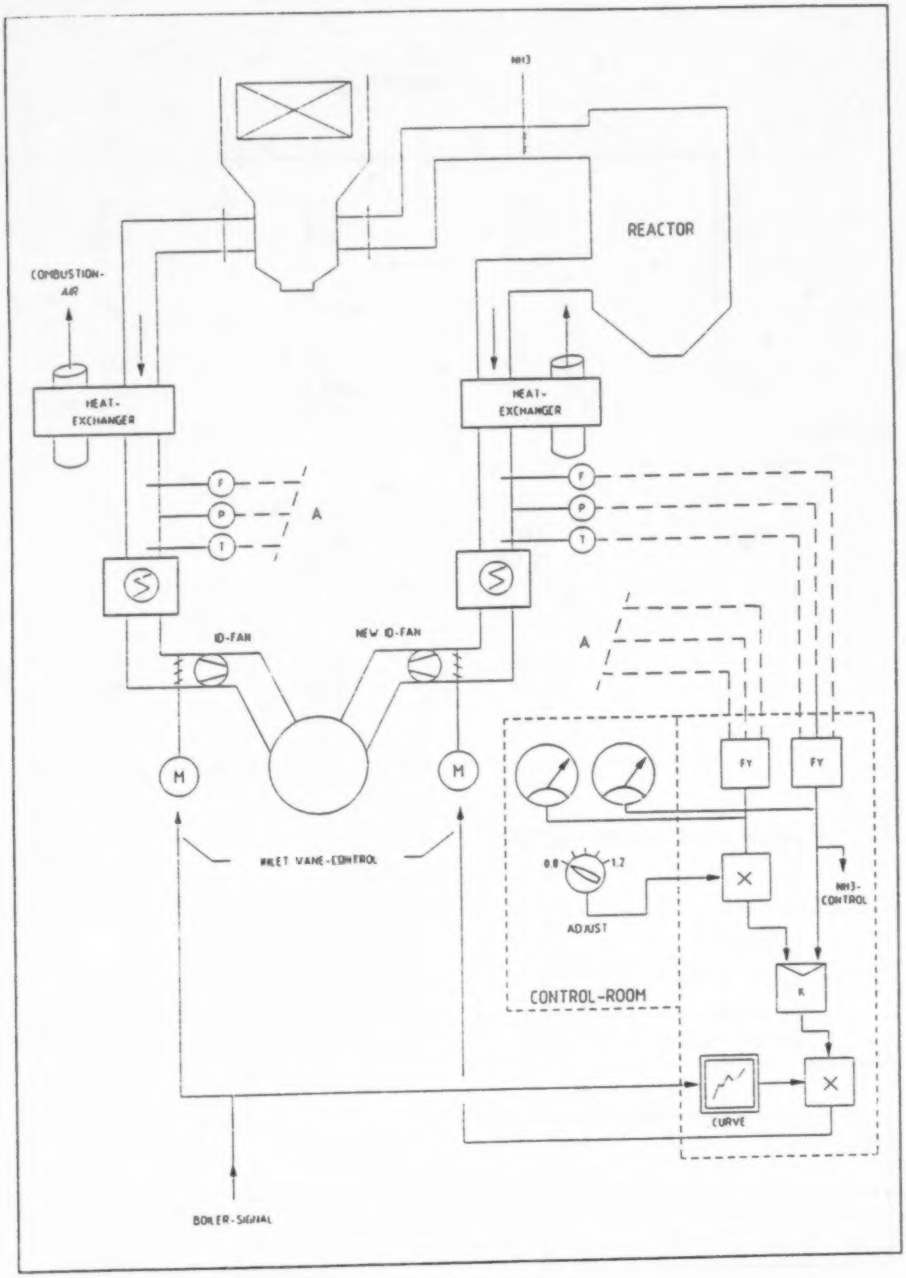


Figure 15. Integrated control scheme of Denox with boiler.

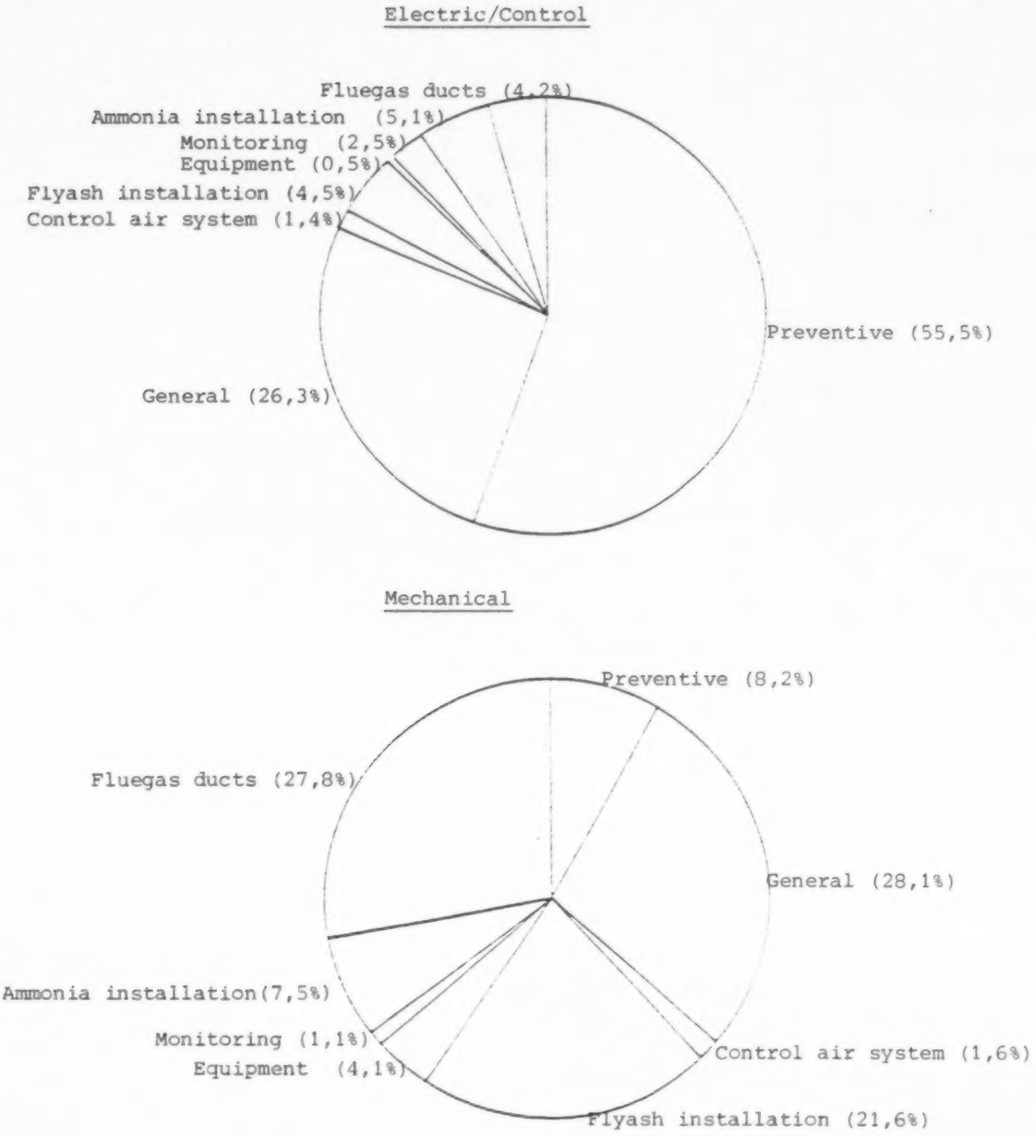


Figure 16. Survey maintenance activities.

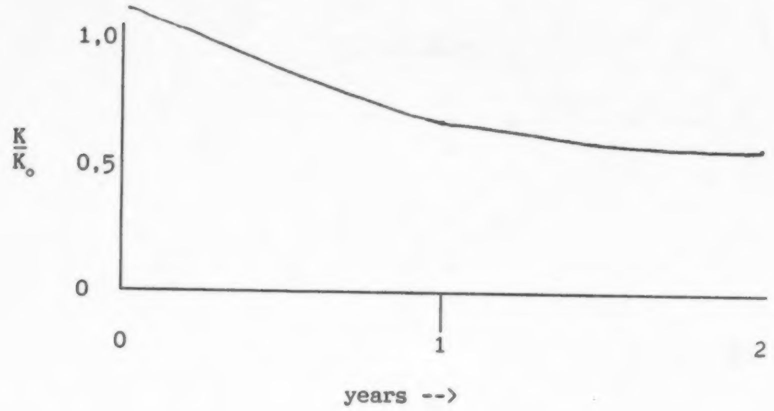


Figure 17. Calculated decrease of catalyst activity.

Table 1

TYPICAL OPERATING DATA
(taken from plant monitoring equipment)

		lowest value	average value	highest value
Temperature				
1. Fluegas after fluegas mixer	°C	347	355	364
2. Fluegas before reactor	°C	339	346	355
3. Fluegas after reactor	°C	336	347	355
4. Fluegas after air preheater	°C	136	147	156
5. Mixture air ammonia	°C	17	28	34
Pressure/pressuredifference				
1. Inlet fluegas pressure	mbar	957	978	996
2. Pressure fluegas after reactor	mbar	951	972	990
3. p reactor (dummy+cat layers)	mbar	5,0	6,1	7,8
4. p NH_3 dosing equipment	mbar	55,1	56,8	59,6
5. p air preheater	mbar	6,5	7,4	8,6
Flows				
1. Fluegas	m^3/h	194406	204268	213875
2. Ammonia	m^3/h	27,2	25,5	53,9
3. Air	m^3/h	2455	2508	2613
Gasanalyses				
1. O_2)	%	2,1	3,3	5,6
2. SO_2) before the reactor	ppm	288	516	653
3. NO)	ppm	203	348	401
5. NO)	ppm	14	52	119
6. NO_2) after the reactor	ppm		10	
7. SO_3)	ppm	6,5	12,3	14,5
Vibration ID fan	mm/s	0,7	1,8	2,6
Power consumption				
1. ID fan	kW	238	259	288
2. Ammonia system	kW	2	5	9
3. Air fan	kW	8	13	16
1. NOx removal	%	74,8	84,7	100,0
2. Total power consumption	kW	253	276	309
3. Ammonia consumption	**kg/h**	**20,31**	**33,75**	**40,12**

Table 2

Δ P OVER CATALYST LAYERS

Operating hours	Reactor layer	Δp in mbar
2500	dummy layer	0,2
2500	cat. layer 1	2,0
2500	cat. layer 2	1,7
2500	cat. layer 3	2,0
4500	cat. layer 1	1,5
	cat. layer 2	1,9
	cat. layer 3	1,4

Table 3

ANALYSIS OF FLYASH WITHOUT AND WITH DENOX

		µg/g	%				%						mg/g
Component	pH	NH_4^+	S	Al_2O_3	CaO	Fe_2O_3	K_2O	MgO	Na_2O	P_2O_5	SiO_2	TiO_2	F
Flyash without denox	9,1	8,8	0,12	32,1	2.36	6,11	1,37	0,81	0,36	0,82	50,2	1,24	0,13±0,01
Flyash after denox	7,5	7,0	0,27	33,7	2,18	5,72	1,58	0,89	0,48	1,24	51,2	1,23	0,18±0,01
Flyash without denox	9.3	4,2	0.16	27.5	2.03	6.93	2.26	1.30	0.35	0.32	52.1	1.02	0,14±0,01
Flyash after denox	8,2	6,2	0,26	28,0	1,91	6,68	2,40	1,26	0,44	0,43	50,9	1,03	0,22±0,01
Average sample from silo without denox	9,4	3,0	0,16	26,6	2,12	6,92	1,62	1,26	0,60	0,55	55,6	0,93	0,10±0,01
Average sample from silo after denox	9,2	3,8	0,18	28,5	2,13	6,79	1,46	1,10	0,46	0,70	53,7	1,00	0,10±0,01

Coal analysis	Average sample 25-01 - 29-01-88	
Bound water	1,6	%
Total water	7,9	%
Ash	9,0	%
Volatiles	29,0	%
Heat value	28,5	MJ/kg
Heat value (calculated)	27,4	MJ/kg
S	0,7	%
C	70,2	%
H	4,5	%
N	1,4	%
Cl	0,09	%
O	6,2	%
F	28	µg/g

OPERATING EXPERIENCE OF SCR SYSTEMS
AT EPDC'S COAL FIRED POWER STATION

by: Tatsushi Mori and Noriyuki Shimizu
Thermal Power Department
Electric Power Development Co., Ltd.
Tokyo, Japan 104

ABSTRACT

Selective catalytic NOx reduction (SCR) system has been installed at Takehara coal fired No. 1 Unit (250 MW) and No. 3 Unit (700 MW) since July 1981 and March 1983 respectively, and is being installed at Matsuura coal fired No. 1 Unit (1,000 MW) which will be commissioned in July 1990. The SCR systems at Takehara No. 1 and No. 3 Units have been operated in good condition through catalyst addition and/or replacement. This paper refers to the current operating experience and inspection results of the SCR systems at Takehara No. 1 and No. 3 Units. The procedure of catalyst addition and replacement is also described. In addition outline of Matsuura No. 1 SCR system is introduced. Furthermore, SCR cost analysis is reviewed based on the latest information. In the final section, EPDC's R&D activity on SCR catalyst is presented.

1. INTRODUCTION

Regulations currently in force on power stations in Japan as to air pollutant emissions include national laws (Air Pollution Control Law), prefectural ordinances and individual agreements made with concerned municipalities (agreements on environmental preservation). Among these three kinds of regulations, prefectural regulations are generally stricter than the national laws, and regulations specified in agreements with concerned municipalities are stricter than prefectural regulations. This means that emission levels are practically regulated by agreements with concerned municipalities. Historically speaking, in addition, the laws have been revised several times for stricter regulations, and regulations agreed in agreements have tended to be stricter one after the other although local characteristics affect such agreements much.

As for NOx emission, one of the air pollutants emitted from power stations, combustion methods were improved at initial stages by using the two stage combustion method, low NOx burners and their improved versions. It was generally recognized, however, that such methods as suppression of NOx generation would be inadequate when emission standards got stricter than the 100 to 200 ppm level. Technical development of flue gas denitrification processes then started. Currently, SCR process, which is one of the dry flue gas denitrification processes, is used widely at thermal power stations in Japan mainly because of its advantages that the system is simple and that it

Preceding page blank

produces no byproducts. As of March 1988, the SCR system is used at thermal power stations of which generation capacity amounts to 36.4 GW, corresponding to 37% of the total thermal power generation capacity of 99.7 GW in Japan. As for coal fired power stations among them, the SCR process is employed at 22 units, which corresponds to 46% of all coal fired units of 48. Counting by the power generation capacity, the SCR process is used for facilities of 6.2 GW, which corresponds to 54% of the total coal fired power generation capacity of 11.4 GW.

The SCR system is classifiable into a low dust and a high dust systems as seen in Figure 1. This distinction comes from the location of the SCR, which is downstream or upstream of ESP in the flue gas flow. The ESP therefore is a hot side ESP for the low dust SCR system, and a cold side ESP for the high dust SCR system. Either process has its own merits and demerits, but both of them have been employed actually for coal fired power generation, and they are operating well. EPDC employs the low dust system for pulverized coal firing power plants. Note that the systems shown in Figure 1 include a flue gas desulfurization system which is in general use in Japan.

Ash of imported coals of low sulfur content used in Japan shows high electric resistances of more than 10^{12} ohm·cm at temperatures around 150°C corresponding to the temperature range of the cold side ESP. The dust collection efficiency of the ESP is deteriorated in such cases, and a larger dust collection area, i.e., a larger ESP is required to compensate for the low efficiency. The electric resistance of such ash, however, lowers to 10^{10} ohm·cm or lower around 350°C, which corresponds to the temperature range of the hot side ESP, and a favorable dust collection efficiency is assured. This means that the use of a hot side ESP, i.e., the use of the low dust SCR system, allows to use a wider variety of imported coals, and it provides a higher flexibility in procurement of overseas coals.

EPDC employed the low dust system in the SCR demonstration test from the reason given above and considering the results of the pilot plant tests which EPDC carried out in order to study SCR systems and catalysts at its power plants from 1976 to 1982 in cooperation with five representative SCR manufacturers.

Fully funded by the Government, EPDC carried out an SCR demonstration test at its Takehara No. 1 Unit (250 MW, PCF) for a year from July 1981. The demonstration plant was the first SCR system which treated all flue gas of a coal fired power unit. The system consisted of two trains of SCR, and catalysts supplied by two SCR manufacturers were used as selected in the preceding pilot plant test. The demonstration test ended with fruitful results. The SCR system of Takehara No. 1 Unit is operating in good condition since then as a commercial system with addition and replacement of catalyst. Results of the demonstration test and findings obtained through operational experiences thereafter were applied effectively to construction of Takehara No. 3 Unit (700 MW, PCF; full flue gas treatment by SCR). The SCR system of Takehara No. 3 Unit is operating well since its start of operation in March 1983 with one addition of catalyst since then. Those experiences are further reflected on Matsuura No. 1 Unit (1,000 MW, PCF; full flue gas treatment by SCR) which is currently under construction. The SCR system of the unit to be completed in July 1990 will be the largest in the world as an SCR system for coal fired power plant.

2. EXPERIENCES IN SCR OPERATION AT TAKEHARA NO. 1 AND NO. 3 UNITS

2.1 Outline of SCR

Figure 2 shows a view of the SCR system of Takehara No. 3 Unit (700MW). The SCR system of Takehara No. 1 Unit (250MW) is similar in shape to that of Takehara No. 3 Unit of vertical downflow type.

Table 1 shows current SCR specifications of Takehara No. 1 and No. 3 Units. The SCR system of Takehara No. 1 Unit consists of two trains, "A" and "B". The catalyst for A train is of plate type, and that for B train is honeycomb type. The SCR system of No. 3 Unit also consists of two trains, but both of them use the same plate type catalyst as that for A train of the No. 1 Unit. Although NOx concentrations at SCR inlet and outlet are different between No. 1 and No. 3 Units, NOx removal efficiency is the same value of 80%.

2.2 SCR Operation

Figure 3 shows records obtained at start up operation of Takehara No. 3 Unit. After the start of the boiler, ammonia is not injected until the flue gas temperature exceeds 300°C. Below that temperature, denitrification reaction rate is very low, and ammonia, if injected, reacts with SO_3 in flue gas and produces ammonium sulfate compounds. Such ammonium sulfate compounds deposit on catalyst surfaces deteriorating the catalyst activity. When the flue gas temperature exceeds 300°C, denitrification reactions occur by injection of ammonia, and the NOx level lowers. Although the time is short, the level of NOx emission is high until service-in of the SCR system. To be able to start the SCR as soon as possible in the plant start up operation is very important. Takehara No. 3 Unit is equipped with a boiler economizer bypass system for this purpose. The damper opening position of this system is programmed as a function of the generator output, assuring to make the SCR inlet gas temperature high quickly for quick SCR service-in even at low generator output by introducing a part of the flue gas directly into the SCR bypassing the economizer.

Figure 4 shows the NOx control system of Takehara No. 3 Unit. Under normal operations, the amount of ammonia injection is controlled so that the NOx concentration at SCR outlet is 50 ppm. Figure 5 shows operation records obtained during a load change. Note that the outlet NOx concentration has been set lower in order to supress peak NOx concentrations during load change below the operational guide line of 60 ppm. It is also possible to control the NOx removal efficiency by setting NH_3/NOx mole ratio.

EPDC carries out SCR performance tests before and/or after the periodical inspections which are conducted annually as specified by laws. Tables 2, 3 and 4 show SCR operational data obtained from the recent performance tests. The SCR systems have operated in stable condition as seen from the data.

2.3 SCR Performance Change in Time

The denitrification efficiency depends also on the NH_3/NOx mole ratio. If the catalyst activity deteriorates therefore, the denitrification efficiency lowers, unreacted ammonia increases even for ammonia injection of the same NH_3/NOx mole ratio. It is possible therefore to check the changes in SCR performance by measuring unreacted ammonia concentration under the same flue gas conditions and the same denitrification efficiency. Figures 6, 7 and 8 show changes in unreacted ammonia concentration measured in the SCR performance tests carried out at the Takehara No. 1A, 1B and No. 3 SCRs. Figures indicate that the slip ammonia increases gradually due to the performance deterioration of SCR caused by gradual deactivation of catalyst in time and that the slip ammonia drops due to the improved performance of SCR by addition or replacement of catalyst.

Ammonium sulfate compounds which come from unreacted ammonia through SCR cause AH clogging and fan vibration. EPDC sets the maximum operating concentration of slip ammonia to be 5 ppm for Takehara No. 1 Unit and 4 ppm for Takehara No. 3 Unit from experiences in their operation. Figure 9 shows relations between the concentration of slip ammonia and the AH washing interval. Correlations between them are obvious, and AH washing frequency is roughly once per six months for each maximum operating concentration of slip ammonia. This means that one washing in a year between periodical inspections is adequate for AH maintenance. One thing to be noted on this matter is the shorter AH washing interval of the No. 3 Unit for the same concentration of slip ammonia compared with the No. 1 Unit. It may come from the remodeling of the AH of No. 3 Unit which was made after one year from the start of operation in order to burn high moisture content coal. The temperature distribution of AH elements along gas flow changed by the remodeling and the temperature range where ammonium sulfate compounds deposit moved toward upstream of gas flow, that is, to the intermediate portion of AH. The soot blower capacity was intensified to cope with this situation, but its effect seems still weak relatively.

The reason for using not the catalyst activity itself but the concentration of slip ammonia as the control value for SCR operation comes from the fact that the decrease in NOx removal efficiency, i.e., increase in NOx at SCR outlet, which comes from deterioration of catalyst activity in time can practically be taken care of by increasing the amount of ammonia injected. Therefore the concentration of slip ammonia is controlled on the SCR to prevent cloggings and vibrations of downstream facilities which are more serious for the plant operation.

EPDC periodically measures changes in the catalyst activity of actually installed sample catalyst as an aid for SCR performance management in addition to the control of slip ammonia described above. Figure 10 shows such an example of changes in activity of sample catalysts. The figure indicates that the deterioration of catalyst activity is rather slow after the initial period. Note that direct comparison among activity test results of sample catalysts for Takehara No. 1 A, No. 1 B and No. 3 SCRs is not appropriate due to different test conditions.

2.4 Catalyst Addition and Replacement

Catalyst additions and replacements have been made on Takehara No. 1A, 1B and Takehara No. 3 SCRs.

For Takehara No. 1A SCR, catalyst was added at the periodical inspections of 1983 and 1985, i.e., two years and four years after the start of operation of July 1981 respectively. The amount of catalyst added at each addition was 16.5% of the original volume. Such additions were made because it was estimated from the trend in the concentration of slip ammonia that the AH washing frequency of more than once a year would be required if the SCR performance were not improved at such occasions. As shown in Figure 10, the rate of deterioration in catalyst activity is slow, and EPDC decided not to replace old catalyst but to add new catalyst to effectively utilize the activity of existing catalyst, thus achieving a higher SCR economy.

Catalyst amounting 12.5% of the original volume was added also for Takehara No. 3 SCR in the similar procedure at the periodical inspection of 1987, i.e., four years after commissioning in March 1983, because the primary AH washing frequency had increased to once per three months. Figure 11 and Photograph 1 show mounting of additional catalyst.

By such additions of catalyst, the rate of slip ammonia decreased as shown in Figs. 6 and 8, and the AH washing frequencies have decreased to levels where AH washing is made only at every periodical inspection for the No. 1A and once at every periodical inspection and once between inspections for the No. 3 Unit.

For the No. 1B SCR, on the other hand, a catalyst addition amounting 30% was carried out one year after commissioning in July 1981. The SO_3 conversion rate of the catalyst was rather high resulting in a high frequency of AH washing, and the tube type catalyst was replaced completely with honeycomb type catalyst at the periodical inspection of 1985, i.e., four years after commissioning. As shown in Figure 7, the concentration of slip ammonia is extremely low since the replacement, and AH washing is made only at each inspection.

EPDC manages catalyst addition or replacement schedule based on the trend of slip ammonia concentration obtained by the SCR performance tests. And the result of performance tests on the sample catalyst is considered also for the management. Figure 12 shows schematic diagram of the SCR performance management.

2.5 Inspection of SCR

The SCRs of Takehara No. 1 and No. 3 Units have been subjected to inspections at each periodical inspection of the plants. At the SCR inspection, accumulation of dust on catalyst layers, support beams and baffle plates, wear, deformation and corrosion of catalyst, and condition of ammonia injection nozzles are checked visually. Photograph 2 and Figure 13 show a state of dust accumulation on catalyst layers observed during inspection of the No. 1 SCRs. It has been confirmed that the accumulation of dust of the level shown in the photographs and the figure does not affect the SCR operation. Such dust, however, is removed during inspection. No major problems have been found in recent inspections, and SCR systems are operating well continuously without requiring any repairs except those which are made during periodical inspections.

2.6 Facilities Downstream SCR

Flue gas from boilers contains a small amount of SO_3 generated during combustion. The concentration of such SO_3 is on the order of 1% or less of the SO_2 concentration although it depends on the boiler type. In addition, the catalyst of the SCR converts a part of SO_2 into SO_3. A part of ammonia injected in the SCR, on the other hand, passes the SCR unreacted with NOx. Such slip ammonia and SO_3 in the flue gas react and cause deposits of ammonium hydrogen sulfate and ash compounds on downstream facilities existing in low temperature ranges such as AH and fans. These deposits then cause troubles such as clogging or vibration. The use of low SO_3 conversion rate catalyst and suppression of slip ammonia therefore are important factors for suppression of adverse effects due to ammonium sulfate compounds on downstream facilities.

For low dust SCR systems, catalyst with low SO_3 conversion rate of 0.5% or less is generally used and SCRs are operated with the maximum value of around 5 ppm for slip ammonia. These measures have been effective for reducing AH clogging at Takehara power station as well.

Table 5 shows differential pressure change before and after AH washing. The table indicates that washing of AH is effective for cleaning the clogged AH. As seen in the case of Takehara No. 3 Unit, however, the washing of a secondary AH requires more than 10 hours, about 1,000 m^3 of washing water and waste water treatment, resulting decreased plant availability and increased maintenance costs. The selection of AH element shapes which prevent deposit accumulation and the selection of soot blower type and its operation schedule become important considerations to be given in the design and operation of the AH. As shown in Table 6, these considerations have been taken into account for Takehara No. 1 and No. 3 Units.

As for the BUF, which is a boost up fan for FGD system, among fans existing in downstream of the SCR, those of Takehara No. 1A and 1B have been cleaned frequently in recent years to cope with actual and possible vibration. The cause of the increase in vibration is unbalanced deposits on the impeller of BUFs. The relation between the deposit and the slip ammonia is not clear now, and it would be a future study item. The BUFs of Takehara No. 3 Unit have different type impeller and no specific problems exist without dust deposits.

For other downstream facilities of SCR such as IDF, FGD, Gas/Gas heat exchanger and FGD wastewater treatment system, no problems specifically ascribable to SCR have occurred.

3. CONSTRUCTION OF LARGE-SCALE SCR

EPDC has employed the low dust SCR as the denitrification system for Matsuura No. 1 Unit (1,000MW) which is under construction and scheduled to start its commercial operation in July 1990. The decision comes from the use of the hot side ESP for collecting fly ash effectively for a wide variety of overseas coals. It goes without saying that the decision was made based on the huge data obtained through operation of hot side ESPs at Matsushima No. 1 and No. 2 Units and Takehara No. 3 Unit covering a time span of more than 8 years, experiences in the operation of low dust SCRs at Takehara No. 1 and No. 3 Units and results of economical evaluation of the whole flue gas treatment system for Matsuura No. 1 Unit including ESP, SCR, FGD and AH as well.

An overview of Matsuura No. 1 SCR is given in Figure 14 and Table 7.

Points of considerations taken into account in the design of Matsuura No. 1 SCR from experiences in operation of Takehara No. 1 and No. 3 SCRs include the following:

- Selection of optimum space velocity

- Additional catalyst space allowing for catalyst volume of 25%

- Suppression of dust deposits

  Distance between catalyst layers, distance between beam and catalyst layer, shape of baffle plate and employment of guide plate

- Improvements in the control system

The SCR plant of Matsuura No. 1 Unit will be the world's largest one when completed.

4. SCR COST

It has been a general understanding in Europe and the U.S. that the SCR system is rather costly. EPDC, however, has demonstrated that the SCR is rather attractive in cost through experiences in construction and operation of SCR systems for Takehara No. 1 and No. 3 Units.

An example of economic evaluation for a new 350MW SCR system is presented here. Table 8 shows premises employed for the economic evaluation. The unit is assumed to be of middle size for base load operation. The coal characteristics are those typical for coals used at imported coal fired power stations in Japan. The SCR is a low dust type according to experiences at EPDC, and NOx concentrations at SCR inlet and outlet are based on those of Matsuura No. 1 Unit. As for the catalyst life, this example assumes that the whole catalyst is replaced at a cycle of 4 years, which has a large margin on the safety side compared with the catalyst life experienced at Takehara No. 1A and Takehara No. 3 SCRs. As for the economic indices, the exchange rate of 130 yen/$ is used, and the discount rate of 10%, which is typical for Japanese electric utilities, is used. As for the plant life, it is assumed to be 20 years, which is more practical than the depreciation period of 7 years under taxation laws in Japan.

Table 9 shows the construction cost and the leverized bus-bar cost calculated from the premises described above. The construction cost and the bus-bar cost are as attractive as $71/kW and 3.5 mills/kWh respectively. As described in INTRODUCTION, SCR systems are widely used in Japan. Information which have been accumulated through actual construction and operation of SCR plants are dependable and uncertainty factors which may lead to a large contingency fund are minimal. In addition, the catalyst performance has been improved gradually as seen from an example of the honeycomb type catalyst used for the replacement at Takehara No. 1B SCR. Further improvements in economy are expected for the future through technical innovations and competitions among manufacturers.

5. R&D ON SCR CATALYST

The catalyst life management is an important factor for stable operation of SCR plants. EPDC has been conducting various tests for evaluation of catalyst performance and clarification of factors for catalyst activity deterioration at its Engineering & Research Institute using catalyst test equipments since 1985, and the catalyst life management is being carried out taking results of such tests into account in addition to the results of performance tests conducted at actual SCR plants.

The catalyst activity test equipment is outlined in Figure 15. Various catalyst samples such as plate type and honeycomb type catalyst samples from actual SCR systems are tested using both this equipment and other analysis devices in order to determine the catalyst activity, establish the method for catalyst life forecast and clarifiy the factors which cause the catalyst activity deterioration. These studies are summarized in Table 10.

Results in the R&D activities up to now are as follows. In the field of determination of sample catalyst activities, the selection of standard conditions such as gas temperature, gas composition, NH_3/NO_x mole ratio and area velocity have been decided in order to measure the NO_x removal efficiency and the SO_3 conversion rate by the catalyst activity test equipment. Based on such achievements, we plan to continue investigations to establish the method for catalyst life forecast.

As for the factors which cause catalyst activity deterioration, followings have been found.

- The reduction in specific surface area leads to catalyst activity deterioration.
- As to the change in pore size distribution in low dust plate type catalysts, pores of size around 50Å in diameter decrease while the ratio of pores of intermediate sizes around 100Å in diameter increases.
- From the adherent material analysis no attachment of poisoning alkali metal elements such as Na and K are recognizable on the surface of sample catalysts as far as being analyzed by a electron probe micro analyzer (EPMA) although dust has deposited on the surface. Forced poisoning tests on catalyst samples have revealed, in addition, that the dust is somewhat responsible for catalyst activity deterioration and that the effect of potassium is large among alkali metals.
- As for the surface conditions, the attachment of dust to catalyst surface depends on the catalyst type and the place of catalyst installation in SCR reactor.
- As for the crystal structure, no change has been recognizable by X-ray analysis.

From the test results above mentioned, the change in catalyst surface conditions such as specific surface area and pore size distribution have close relation to catalyst activity deterioration in the case of SCR catalysts of Takehara Power Station.

6. CONCLUSION

EPDC has been playing pioneering roles among electric power utilities in Japan in the development and utilization of the SCR process for coal fired power plants since 1976 by its steady accumulation of experiences represented by the pilot tests, demonstration tests and more than 6 years of commercial operations of SCR plants. The SCR process is now used widely at about half of all coal fired power stations in Japan, and the SCR system now belongs to a well-matured technology in Japan. EPDC envisions for larger SCR systems, and a world's largest SCR unit will be completed in 1990. It has been demonstrated that SCR system is attractive in cost, and the system is getting more economical through technical innovations and competition among SCR manufacturers. EPDC continues its efforts on improvement of the SCR system including the establishment of a method for catalyst life management and further improvement of system economy.

REFERENCES

1. "NOx Removal from Flue Gas", Y. Nakabayashi, Conference on "The Role of Coal in the Swedish Energy System, Possibilities and Limitations", Södertälje, Sweden, October 1988

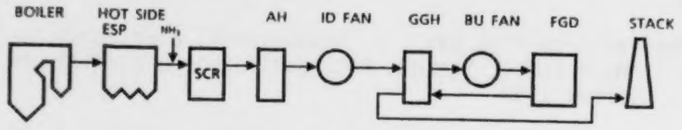
2. "Flue Gas Treatment Facilities Operation Experience", T. Miyasaka, the same conference as Reference 1

3. "Design of Flue Gas Treatment Facilities", T. Kainuma, the same conference as Reference 1

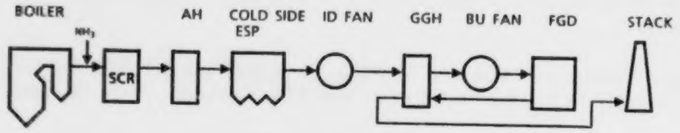
4. "Current Status of SCR in Japan", Y. Nakabayashi and R. Abe, 1987 Joint Symposium on Stationary Combustion NOx Control, New Orleans, U. S. A., March 1987

5. "Updated Technical and Economic Review of Selective Catalytic NOx Reduction Systems", J. E. Damon and D. V. Giovanni, the same joint symposium as Reference 4

6. "The Operation Results of DeNOx System (SCR) for Unit No. 3 (700 MW) at Takehara Thermal Power Station, Japan", J. Watanabe, NOx Symposium Karlsruhe 1985, Karlsruhe, West Germany, February 1985



LOW DUST SCR SYSTEM



HIGH DUST SCR SYSTEM

Fig. 1 Type of SCR System

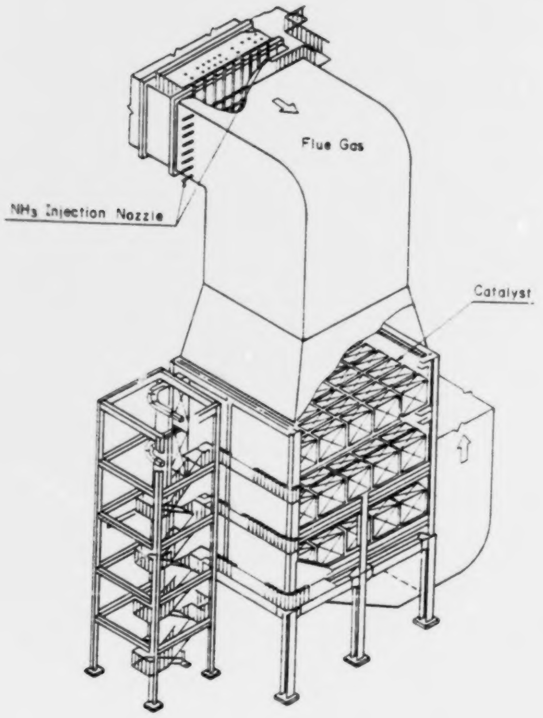
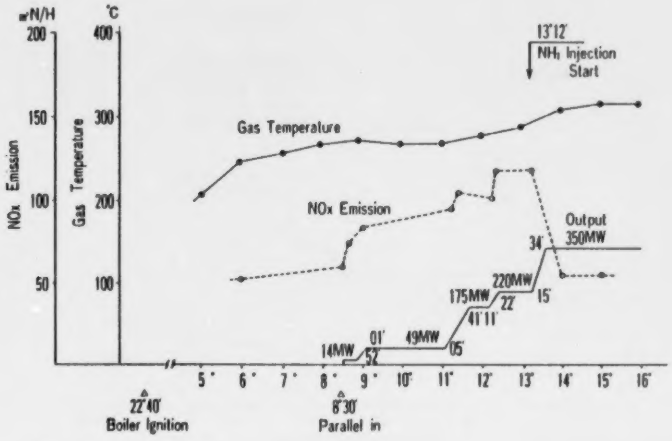
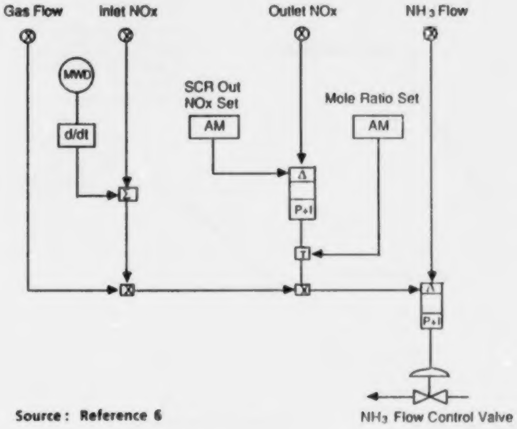


Fig. 2 Takehara #3 SCR Reactor



Source : Reference 6

Fig. 3 Start Up Record of Takehara #3



Source : Reference 6

Fig. 4. NOx Control System at Takehara #3

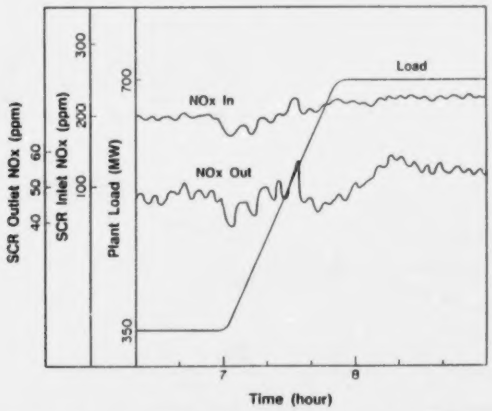
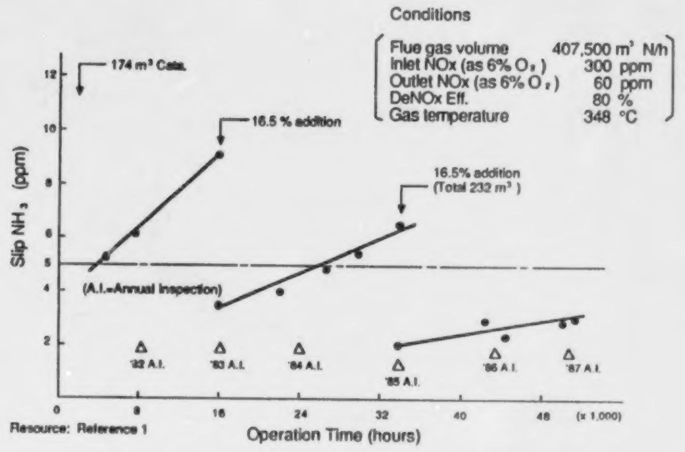
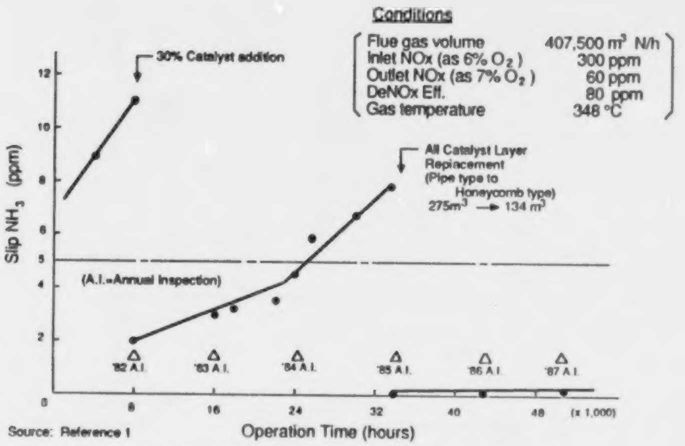


Fig. 5 NOx Control during Load Change at Takehara #3



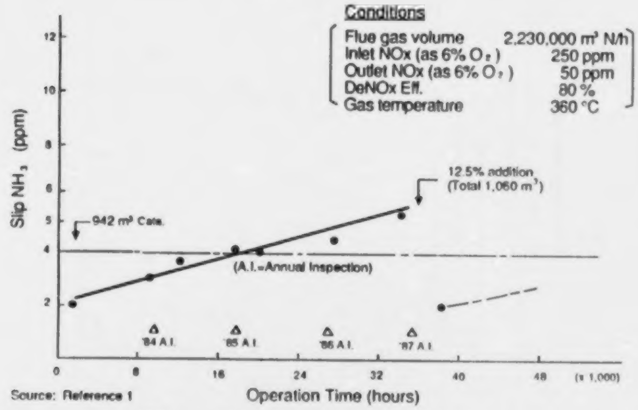
Resource: Reference 1

Fig. 6. Slip NH_3 Trend at Unit No. 1 A-train



Source: Reference 1

Fig. 7. Slip NH_3 Trend at Unit No. 1 B-train



Source: Reference 1

Fig. 8. Slip NH_3 Trend at Unit No. 3

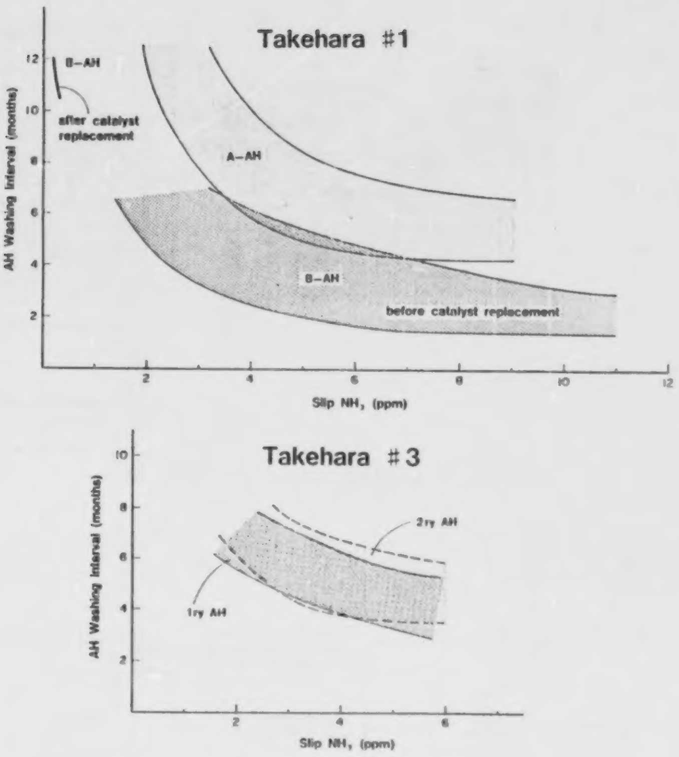


Fig. 9 Slip NH_3 vs. AH Washing Interval

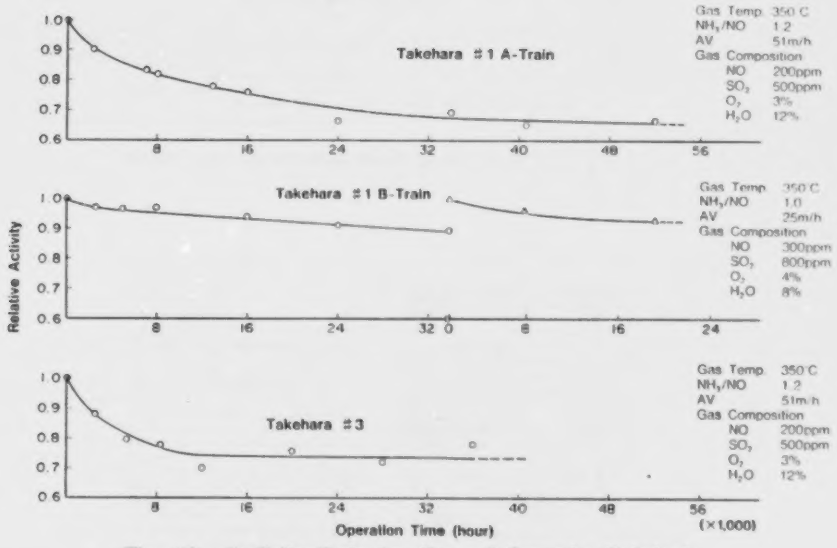


Fig. 10 Activity Deterioration of Sample Catalyst

Note: Direct comparison among above three graphs is inappropriate

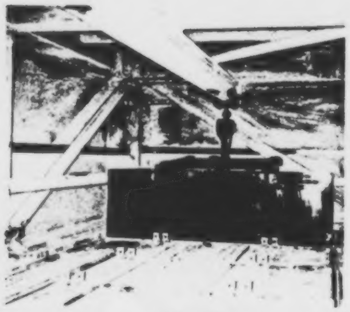


Photo. 1

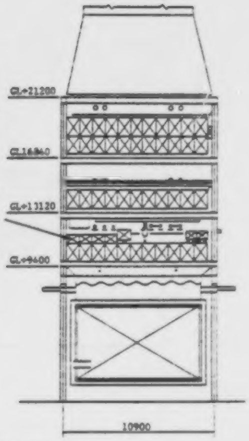
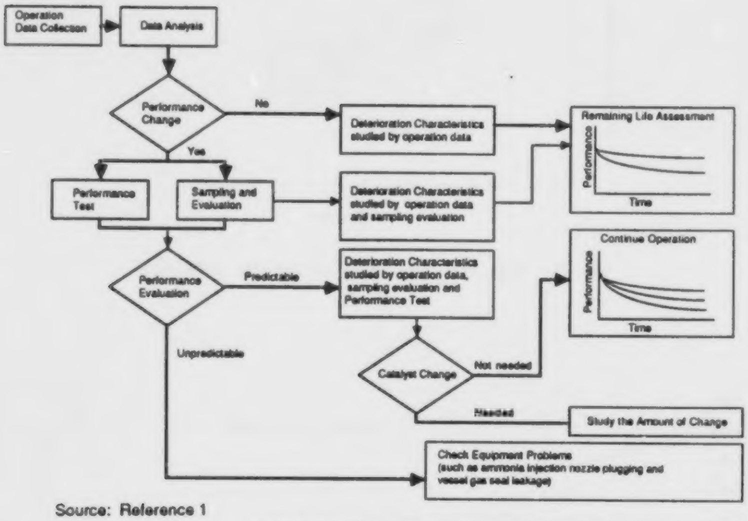


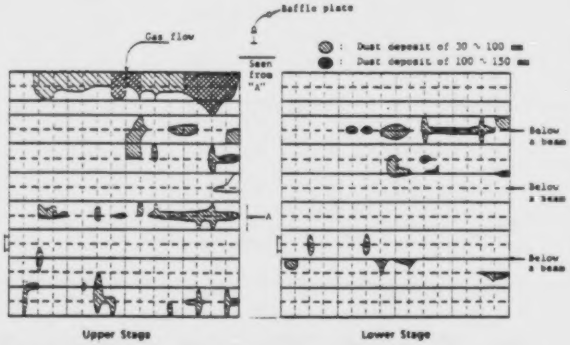
Fig. 11 Additional Catalyst at Takehara #3



Operation Data Collection
Data Analysis
Performance Change
No
Yes
Deterioration Characteristics studied by operation data
Remaining Life Assessment
Performance
Time
Performance Test
Sampling and Evaluation
Deterioration Characteristics studied by operation data and sampling evaluation
Continue Operation
Performance
Time
Performance Evaluation
Predictable
Deterioration Characteristics studied by operation data, sampling evaluation and Performance Test
Unpredictable
Catalyst Change
Not needed
Needed
Study the Amount of Change
Check Equipment Problems (such as ammonia injection nozzle plugging and vessel gas seal leakage)

Source: Reference 1

Fig. 12. SCR Catalyst Performance Control Flow Diagram



Source : Reference 2

Fig. 13 Dust Deposits on Catalyst Layers at #1 - A Train

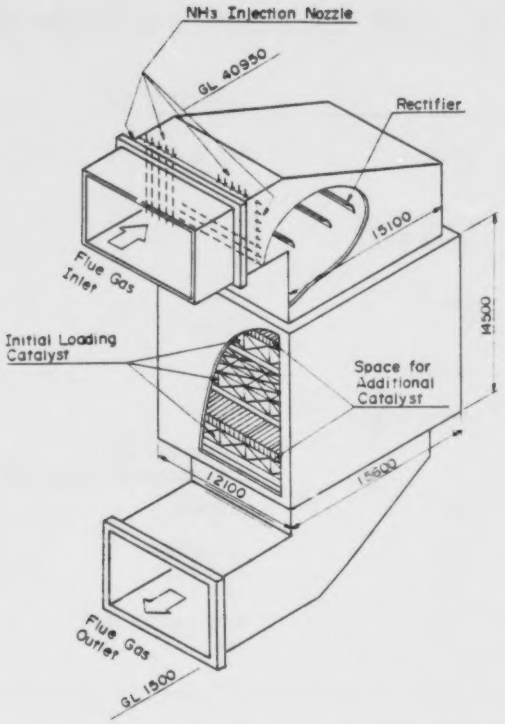


Fig. 14 Matsuura # 1 SCR Reactor

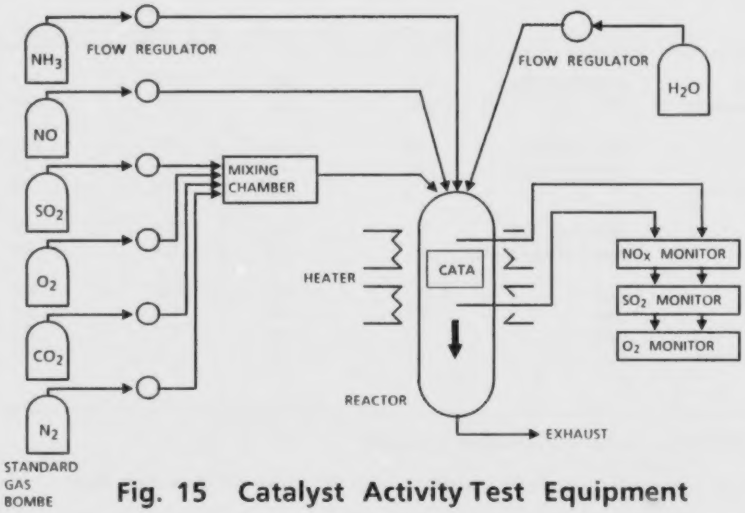


Fig. 15 Catalyst Activity Test Equipment

Table 1. SCR Specifications of Takehara #1 and #3

Train		Takehara #1 A/B	Takehara #3
Gas Volume	m^3 N/h	407,500 / 407,500	2,230,000
Gas Temperature	°C	329 - 348	360 - 380
NOx In	ppm (6 % O_2)	300	250
NOx Out	ppm (6 % O_2)	60	50
DeNOx Efficiency	%	80	80
SOx In	ppm	1,850	1,000
SO_3 Conversion	%	0.5 max.	0.5 max.
Dust In	mg/m^3N	100	100
Slip NH_3	ppm (6 % O_2)	3.7/4.0	3.6
Catalyst Type	---	Plate (10mm pitch) /Honeycomb (6mm opening)	Plate (10mm pitch)
Catalyst Volume	m3	232/134	1,060
Space Velocity	1/h	1,760/3,037	2,110
Area Velocity	m/h	8.7/6.5	10.4
Linear Velocity	m/s	4.8/5.2	6.9
Reactor Dimension	m	8.5W x 8.5D x 10.8H	10.9W x 12D x 13H
Catalyst Stage	---	4 / 3	4.5
Train	---	1 / 1	2

Table 2. Takehara #1-A SCR Performance Test Result

		Aug. 1985	Dec. 1985	Nov. 1986	Oct. 1987	Feb. 1988
Gas Volume	x 1,000 m^3 N/h	404	389	399	396	398
Gas Temperature	°C	343	344	352	341	348
NOx In	ppm (6 % O_2)	266	287	271	238	252
NOx Out	ppm (6 % O_2)	55	51	68	53	52
DeNOx Efficiency	%	79	82	75	78	79
Slip NH_3	ppm (6 % O_2)	7.2	2.3	1.3	2.8	2.5
Slip NH_3	ppm (design basis)*	6.6	1.9	2.9	2.7	3.0
SOx In	ppm	1,520	1,420	1,240	1,420	1,050
SO_3 In	ppm	4.0	4.4	5.3	2.1	3.4
SO_3 Out	ppm	5.0	4.8	5.7	2.5	3.8
SO_3 Conversion	%	0.07	0.04	0.03	0.03	0.04

* : calculated on the design basis described in Figure 6

Catalyst was added in the periodical inspection between September and November, 1985.

Table 3. Takehara #1-B SCR Performance Test Result

		Aug. 1985	Dec. 1985	Nov. 1986	Oct. 1987	Feb. 1988
Gas Volume	x 1,000 m^3 N/h	380	396	411	377	395
Gas Temperature	°C	333	343	354	343	340
NOx In	ppm (6 % O_2)	274	306	283	251	249
NOx Out	ppm (6 % O_2)	75	61	60	45	52
DeNOx Efficiency	%	73	80	79	82	79
Slip NH_3	ppm (6 % O_2)	8.1	0.1	0.1	0.2	0.1
Slip NH_3	ppm (design basis)*	6.8	0.1	0.1	0.2	0.1
SOx In	ppm	1,440	1,490	1,180	1,340	1,210
SO_3 In	ppm	4.3	5.2	4.9	3.2	2.8
SO_3 Out	ppm	19.0	7.6	7.4	3.2	4.6
SO_3 Conversion	%	0.75	0.18	0.21	0.08	0.15

* : calculated on the design basis described in Figure 7

Catalyst was replaced in the periodical inspection between September and November, 1985.

Table 4. Takehara #3 SCR Performance Test Result

		Sept. 1985	Aug. 1986	Aug. 1987	Dec. 1987
Gas Volume	x 1,000 m^3N/h	2,140	2,318	2,346	2,364
Gas Temperature	°C	360	366	365	360
NOx In	ppm (6 % O_2)	246	228	245	226
NOx Out	ppm (6 % O_2)	51	53	45	44
DeNOx Efficiency	%	79	77	82	81
Slip NH_3	ppm (6 % O_2)	2.6	2.4	6.2	2.0
Slip NH_3	ppm (design basis)*	3.9	4.5	5.3	2.3
SOx In	ppm	221	205	405	200
SO_3 In	ppm	1.3	1.0	2.1	2.6
SO_3 Out	ppm	1.7	1.5	3.6	3.4
SO_3 Conversion	%	0.16	0.24	0.37	0.4

* : calculated on the design basis described in Figure 8

Catalyst was added in the periodical inspection between September and November 1987.

Table 5. Pressure Recovery by AH Washing

		Differential Pressure of AH (mmAq)	
		Before Washing	After Washing
Takehara #1	A-AH	90	60
	B-AH	70	55
Takehara #3	1ry AH	114	88
	2ry A-AH	95	70
	2ry B-AH	68	60

Table 6. Basic Consideration for AH Clogging

• AH Element	NF type layer in possible deposit areas
• Soot Blower	Reinforced blower such as retractable, twin or multi nozzle types
• Blowing Schedule	Increased blowing frequency, ex. 6 times/day

Table 7. SCR Specification of Matsuura #1

Design Basis		Max. Gas Vol. / Max. Inlet NOx
Gas Volume	x 1,000 m^3 N/h	3,100 / 3,029
Gas Tempeature	°C	370
NOx In	ppm (6 % O_2)	200 / 250
NOx Out	ppm (6 % O_2)	50
DeNOx Efficiency	%	75 / 80
SOx In	ppm	200 - 1,000
SO_3 In	ppm	3.5 max.
SO_3 Conversion	%	0.5 max.
Dust In	mg/m^3N	100
Slip NH_3	ppm	2/3.5
Catalyst Type	—	Plate (10 mm pitch)
Catalyst Volume	m^3	1,541
Space Velocity	1/h	2,010
Area Velocity	m/h	10
Linear Velocity	m/s	6.5
Reactor Dimension	m	12.1W x 15.6D x 14.5H
Catalyst Stage	—	3
Train	—	2

Table 8. Premises for Economic Evaluation

Plant Generating Capacity	350 MW x 1, new unit
Plant Efficiency	38.3 % (net)
Plant Use Factor	8.6 %
Annual Capacity Factor	70 %
Electricity Transmitted	1,961 GWh/year
Coal Calorific Value	6,200 kcal/kg JIS ad
Sulfur Content	1.2 %
Nitrogen Content	1.8 %
Ash Content	15 %
SCR Type	Low Dust System
NOx In/Out	250/50 ppm (80% DeNOx Efficiency)
Catalyst Life	4 years
Train	2
Ammonia Cost	$850/t
Currency Exchange Rate	Yen 130/$
Discount Rate	10 %
Escalation Rate	0 % pa
Plant Life	20 years

Table 9. SCR Cost [350 MW x 1, new unit, 1989 value, 1$ = 130 Yen]

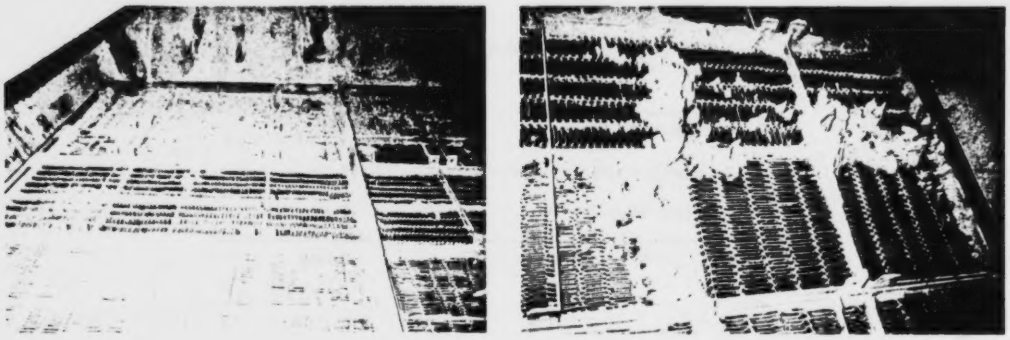
CONSTRUCTION COST	
Reactor and Ducting	$23 / kW
Catalyst	28
Ammonia Facilities	5
Others (Electrical Equipment, C & I, Civil Works)	3
On-Site Engineering & Support Facilities	6
Interest during Construction	4
Home Office Fee	2
TOTAL CAPITAL REQUIREMENT	$71 / kW
LEVERIZED BUS-BAR COST	
Capital	1.5 mills/kWh
Operation and Maintenance	0.4
Catalyst Exchange	0.9
Ammonia	0.5
Other Utilities	0.1
Tax	0.1
TOTAL BUS-BAR COST	3.5 mills/kWh

Table 10. R & D on SCR Catalyst

- Sample Catalyst Activity Test
- Catalyst Life Forecast
- Study on Factors in Catalyst Deactivation

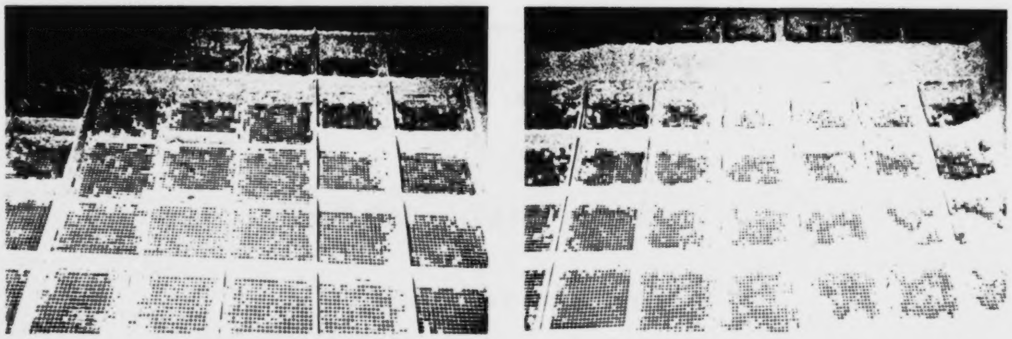
• Specific surface area	N_2 adsorption (BET)
• Pore size distribution	Mercury method
• Adherent material analysis	Atomic absorption analysis
• Surface state	SEM
• Crystal structure	X-ray Analysis

Reproduced from best available copy.



Lightly Deposited Area **Heavily Deposited Area**

Takehara #1 - A Train



Lightly Deposited Area **Heavily Deposited Area**

Takehara #1 - B Train

Photo. 2 Ash Deposits at Takehara #1 SCR

TECHNICAL FEASIBILITY AND ECONOMICS
OF SCR NO_x CONTROL
IN UTILITY APPLICATIONS

C.P. ROBIE
P.A. IRELAND
UNITED ENGINEERS & CONSTRUCTORS INC.
STEARNS-ROGER DIVISION
AND
J.E. CICHANOWICZ
ELECTRIC POWER RESEARCH INSTITUTE

ABSTRACT

An evaluation is presented of the technical feasibility and economics of retrofitting selective catalytic reduction (SCR) technology to one oil and one coal fired power plant. The current status of the technology is assessed based primarily on recent European experience. Costs are included in the analysis for operational effects on downstream equipment. The capital cost ranges from 78 to \$94/kW for the oil case and 78 to \$101/kW for the coal case; the levelized busbar cost ranges from 3.5 to 12.2 mills/kWh for the oil case and 5.2 to 6.6 mills/kWh for the coal case.

INTRODUCTION

Recently proposed acid rain legislation in Congress has focused attention on the cost of SCR NO_x control. In addition, European experience with SCR has expanded the understanding of the cost of this technology. This paper presents an evaluation of the technical feasibility and cost of retrofitting the SCR process for NO_x control to one typical oil-fired and one coal-fired U.S. power plant.

The cases examined in this paper are the first two of six to be examined in a larger study performed for EPRI, assessing the cost and feasibility of SCR. The six cases are defined as follows:

1. Retrofit - oil/gas fired plant
2. Retrofit - tangential, high sulfur coal-fired boiler
3. Retrofit - cyclone, high sulfur coal-fired boiler
4. New plant - low sulfur coal
5. New plant - high sulfur coal
6. Retrofit - high sulfur coal-fired boiler implementing "cold-side" SCR downstream of flue gas desulfurization (FGD) equipment

Complete results for all cases will be presented in an EPRI report anticipated in the fall of 1989.

Regulations in Europe have led to significant application of SCR NO_x control. By 1992 application to over 30,000 MW of capacity is anticipated. Currently, some SCR installations have been in operation for about three years. In addition, numerous European SCR pilot plants have increased the understanding of this technology. Based on this European experience, the following design assumptions were selected for the evaluation:

1. Catalyst life - Several coal-fired European SCR installations have operated for over two years without catalyst replacement and only moderate measured loss in reactivity. A catalyst life of four years for coal-fired plants and six years for oil-fired plants has been used in this evaluation.

2. Catalyst cost - Catalyst costs in Europe have decreased over the past four years by a factor of approximately 2.5 , primarily due to a very competitive supply situation. Accordingly, this evaluation covers catalyst costs from $\$330/ft^3$ to $\$660/ft^3$, covering the range seen in Europe.

3. Ammonia slip - Ammonia slip in European SCR installations is typically specified at 5 ppm, while some utilities recommend even lower levels (2 ppm). For the coal cases, a 5 ppm slip only has been evaluated. A slip of 10 ppm for the oil case was utilized.

4. Space Velocity - Advances have been made in catalyst formulation to minimize SO_2 to SO_3 conversion, to develop smaller pitches and to provide resistance to fouling by trace elements. These various advances are reflected in the space velocities used for the two cases in this evaluation.

CASE DEFINITION

In order to develop a representative cost of retrofitting SCR, a typical existing power plant layout and typical design conditions were selected for each case. Minor modifications were made to provide study cases with broader industry applicability. Definition of the two study cases are summarized in Table 1.

In both cases, the SCR reactor was located above the existing air heaters because of space constraints. The oil case required a high width to length ratio to allow placement of the reactor between the boiler and the stack. Vertical (downward gas flow) reactor configurations were selected for both cases; the coal case because of ash in the flue gas and the oil case due to space constraints. Plans and elevation sketches of the SCR reactors are shown on Figures 1 and 2.

SCR PROCESS DESIGN

To obtain budgetary SCR system costs, a performance specification for the catalyst and reactor supply was developed for each case. The specifications were developed using fuel analyses, plant performance and emissions data from the actual power plant sites. Additionally, emissions performance and ammonia slip requirements were specified for each case as well as certain sensitivities of interest. Three SCR system suppliers provided quotations to these specifications.

The SCR design basis and resultant vendor supplied design data are shown in Table 2. Two cases each for both the oil and coal plants were developed to show the effect of changing the uncontrolled NO_x emission rate (by combustion control techniques) while still meeting the same NO_x emission limit. The NO_x emission limit of 0.03 lb NO_x/ MM Btu for the oil case requires 90% NO_x reduction for case A and 80% for case B. Similarly, the NO_x emission limit of 0.12 lb NO_x/MM Btu for the coal case requires 80% NO_x reduction for case A, and 70% for case B.

A single, vertical reactor was specified for the oil case, while twin (2 x 50%), vertical reactors were specified for the coal case. Both reactor designs include the capacity to add an additional catalyst layer. Typically, the fifth catalyst layer would be added after two years (coal case) or three years (oil case) of process operation. Yearly replacement of a single catalyst layer would begin after four years for the coal case and six years for the oil case.

The reactors were designed with steam soot blowers between each catalyst layer. The soot blowers are recommended in the oil case because of the peaking duty criteria and in the coal case because of fly ash content in the flue gas.

The ammonia storage and supply systems for both cases were designed using a truck unloading station and a storage island providing seven days storage at an MCR rating. Steam vaporizers are utilized for ammonia vaporization and dilution air is provided from the discharge of the Primary Air fans in the coal case and the Forced Draft fans in the oil case. In the oil case, an urban site is assumed and the NH_3 storage island is located below grade.

The low sulfur and ash content of the fuel in the oil case allows selection of a catalyst with a high specific area and high activity which results in a space velocity considerably higher than the coal case.

SCR PROCESS IMPACT

The SCR process, because of its location directly downstream of the boiler and upstream of the air heater, affects every component of the flue gas train and the boiler itself through its effect on the air heater. The degree of its effect varies with power plant configuration, environmental control components, type of fuel, and emission control requirements.

Oil Case Impact

For the oil case, the SCR design impact is summarized on Figure 3. The principal effects are on the boiler, air heater and the requirement for new ID fans. These and other effects are discussed below:

Boiler. The oil-fired power plant selected for analysis utilizes a pressure boiler. That is, forced draft (FD) rather than induced draft (ID) fans are utilized. To accommodate SCR several modifications were implemented.

To maintain the flue gas temperature above about 600°F (minimum recommended SCR operating temperature) over all load conditions, an economizer bypass has been added. The bypass flow will be automatic, controlled off the SCR inlet temperature.

To prevent possible implosion of the boiler, pressure control bypasses have been added to the new ID Fans. The ID Fans will complicate pressure control in the boiler.

Modifications to the air heater will result in a higher flue gas exit temperature, reduced air inlet temperature and reduced plant efficiency. The result will be slightly less generating capacity at MCR conditions.

Air Heater. Formation of ammonium bisulfate (from SCR operation) and its deposition on air heater surfaces requires major modification to the twin, horizontal air heaters.

The cold-end baskets will be replaced with NF (notched, flat) surface. This will result in a higher flue gas exit temperature of approximately 5°F and a loss in boiler efficiency. The cold end basket will be combined with the intermediate NF basket to provide a continuous surface to facilitate cleaning.

High pressure steam soot blowers will be added to both the hot and cold sides of the air heater. The high pressure steam will require replacement of the 24 gage air heater heat transfer surface with 18 gage material.

To provide continuous operation, on-line water washing capability is provided; the water wash is required to clean ammonium bisulfate deposits off heat transfer surfaces. On-line water washing requires adding high pressure water wash assemblies upstream and downstream, air bypasses (from air side to flue gas side) and dampers, and water wash pumps and piping.

To ensure proper flue gas distribution to the air heater, rectifying plates and turning vanes have been added. In addition, the air heater outlet plenum and ductwork are modified to accommodate new ID fans.

ID Fans. The existing FD fans are not capable of overcoming additional flue gas pressure drop associated with the SCR process. Accordingly, new axial ID fans have been added downstream of the existing air heaters. The axial fans provide high efficiency service in the cycling operation specified for this application. Total estimated pressure drop attributable to the SCR operation is 12 " W.C. A contributing factor to the high pressure drop attributable to the SCR process is the increase in the flue gas volumetric flow rate. The volumetric flowrate (downstream of the air heater) increases as a result of higher flue gas temperature, reduced pressure, and increased mass flow resulting from higher air heater leakage and dilution air.

FD Fan. The FD fans will consume slightly more power to account for a higher mass flow rate. The higher mass flow results from a higher air heater leakage rate and in providing dilution for the injected ammonia.

Water Treatment. Introduction of nitrogen species into the air heater wash water requires additional water treatment equipment. Nitrogen species are introduced into the wash water as ammonium bisulfate and sulfates. A nitrification and denitrification biological treatment process is utilized to convert the nitrogen species to free nitrogen.

The discharge from the denitrification process is assumed to be discharged to the existing on-site water treatment equipment.

Coal Case Impact

In the coal case, retrofitting SCR has similar impacts as discussed above for the oil case and additional ones because of the greater complexity of environmental controls. The impacts are summarized on Figure 4.

The principal impacts are on the boiler, air heater and ID fan. Other impacts are on the particulate collection device (ESP), wet limestone flue gas desulfurization (FGD) process, FGD reheat system, waste disposal system and water treatment system.

Boiler. A tangential-fired boiler is utilized in the coal study case. The principal effects of SCR on the boiler will be the loss of overall efficiency and additional control complexity.

Air heater modifications will result in a higher air heater flue gas exit temperature resulting in a reduction of plant efficiency. The result will be a loss in net generating capacity.

Air Heater. Formation of ammonium bisulfate coupled with the presence of fly ash necessitates air heater modifications. The modification to the twin (2 x 50%) trisector air heaters include adding high pressure steam soot blowers at both the cold and hot ends, adding high pressure water wash capability, replacing 24 gage heat transfer surface material with 18 gage, replacing intermediate and cold end double undulating (DU) heat transfer surface with Notched Flat (NF) surface, and adding bypasses and dampers for on-line washing capability.

ID Fan. To overcome additional pressure drop (11" W.C.) associated with the SCR, the existing ID fans were modified. It was assumed that new, larger diameter wheels could be placed into the existing fan housings to overcome the additional static pressure drop. The modifications included replacing the fan wheel, shaft, bearings and motor.

ESP. SCR effects on the ESP include higher volumetric flowrate, higher negative operating pressure, higher SO_3 concentration, higher flue gas temperature and precipitation of ammonium bisulfate on fly ash.

Higher flue gas volume (9.4%) resulting from higher flue gas temperature (20°F), lower flue gas static pressure and increased mass flow due to increased air heater leakage and dilution air will have a significant impact on ESP operation. The increase in flue gas volume results in a reduction of the Specific Collecting Area (SCA) and in a reduction in the concentration of particulate in the flue gas. The result will be that the ESP will require additional power to effect the same particulate removal efficiency.

Greater negative operating pressure could require re-enforcement of the ESP. This effect was not considered in the capital cost analysis.

The SO_3 concentration in the flue gas is estimated to increase by 18 ppm across the SCR. Typically, an increase in SO_3 would be expected to reduce the fly ash resistivity significantly. However, the increase in the flue gas temperature may counteract the effect of the SO_3 increase, possibly producing little net change.

An increase in the flue gas temperature by 20°F results from a loss of air heater performance. The temperature increase will keep the flue gas temperature above the acid dew point therefore not affecting fly ash resistivity significantly.

Ammonium bisulfate precipitation on the fly ash can have a beneficial impact on ESP performance by helping the fly ash agglomerate, preventing reentrainment.

The cumulative effects of all the above could be significant on an ESP. As a result, a test program would be recommended to determine actual design and operations impacts. In this study case it was assumed that the only net effect on the ESP operation was an increase in power consumption by about 12%.

Ash Disposal. Ammonium bisulfate precipitation on the fly ash can have a significant impact on waste disposal or marketing practices. In the case of an Eastern coal with acidic constituents, offgassing of ammonia will not likely occur during waste disposal. However, ammonium bisulfate will offgas ammonia when the pH is raised, and as a result the fly ash may not be a marketable commodity to the construction industries.

FGD/Reheat. The chief effect on the FGD system in this study case is an increase in the water evaporation rate and steam reheat requirement. The higher inlet temperature and higher mass flow rate will result in an increase in water evaporation in the absorber. In this particular case, an increase in the water evaporation rate of approximately 85 gpm will result.

The higher flue gas mass flow and increase in water evaporation will result in a significant increase in steam use by the FGD reheat system (50°F reheat assumed). The increase in mass flow requires approximately 3.7 MM Btu/hr of heat input.

A slight increase in power consumption could occur from having to increase the FGD liquor recirculation rate in order to maintain the same SO_2 removal efficiency. The higher liquor recirculation rate might be required as a result of dilution of SO_2 in the flue gas, and higher flue gas volumetric flow rate (saturated gas flowrate). This effect was not considered in this analysis.

In this case, it is expected that some residual ammonia may be captured by the FGD system resulting in a build-up of ammonium sulfate species in the FGD liquor. Although this may complicate scrubber sludge reuse or disposal, no cost impact has been assigned.

Stack. The increase in the flue gas SO_3 concentration across the SCR could result in increased opacity of the flue gas plume. Recent data from an EPRI sponsored study with a member utility shows a direct correlation between stack opacity and sulfuric acid concentration. To reduce opacity increases, control measures may be required to reduce the SO_3 concentration. A typical method of reducing SO_3 in the flue gas would be to inject NH_3 upstream of the ESP. This impact has not been evaluated in this study, however.

COST DEVELOPMENT

To develop total process capital costs for the oil and coal case retrofits, physical layouts of the ductwork and SCR reactors were developed. From these drawings, lengths of ductwork and structural requirements were estimated.

The operating and capital cost impact of SCR on other plant components was also estimated. For major pieces of equipment, such as the air heaters, ammonia storage system and ID fans, vendors were consulted in developing the cost of the modifications. For smaller equipment items and piping runs, S-R utilized in-house data to arrive at equipment costs.

In developing operating costs, S-R utilized EPRI's Technical Assessment Guide (TAG) to estimate fixed operating and maintenance costs. Variable operating costs were determined by calculating utility and raw material consumption rates. Considered in developing the variable operating costs were the following:

- SCR catalyst replacement
- Ammonia consumption
- Ammonia vaporization steam

- Incremental Sootblowing steam
- Incremental ID fan horsepower consumption
- Incremental FD fan horsepower consumption
- Incremental ESP power consumption
- Water treatment chemicals
- Air heater efficiency loss
- Increased air heater leakage
- Incremental FGD reheat steam consumption
- SCR catalyst disposal
- Incremental fly ash disposal cost

RESULTS

Figures 5 to 8 report the Oil Case cost results; Figures 5 and 6 report capital costs, while Figures 7 and 8 report levelized costs.

- Figure 5 indicates that the Total Capital Requirement (TCR) varies from \$79/kW to \$94/kW. The results indicate that the SCR capital cost required to achieve 0.03 lb/MM Btu is \$7.6/kW less when boiler combustion controls are added to reduce the boiler emissions from 0.30 to 0.15 lb/MM Btu. This results from more catalyst required to achieve the 0.03 lb/MM emission limit at the higher boiler emission rate; the 90% case requires a space velocity of 3370 hr^{-1} versus 3900 hr^{-1} for the 80% case.

- Figure 5 also shows the impact of catalyst cost. Comparing Cases A and C shows that the capital cost required to achieve 90% NO_x reduction can be reduced by \$14.9/kW (16%) if the initial catalyst cost is reduced to \$330/ft^3.

- Figure 6 shows the cost components that make up the TCR for Oil Case A. Total Process Capital (TPC) comprises the largest component. Of the TPC figure, approximately 50% can be attributed to catalyst and reactor cost. It is interesting to note that for a catalyst cost of \$330/ft^3, the TPC figure would be dominated by structural and ductwork costs.

- Figures 7 and 8 report the levelized cost of removing NO_x. Figure 7 presents \$/ton NO_x removed, while Figure 8 presents busbar cost (mills/kWh) associated with SCR NO_x control. Both curves show the strong effect of capacity factor on the cost as well as the effect of a higher uncontrolled NO_x emission rate. Figures 7 and 8 indicate that the lowest levelized SCR cost is for a high uncontrolled NO_x emission rate at a high capacity factor. Cases A and C, at an uncontrolled NO_x rate of 0.30 lb/MM Btu and a 65% capacity factor, exhibit the lowest \$/ton NO_x removed cost of the cases presented.

Figures 9 to 12 report the coal case cost results; Figures 8 and 9 report capital cost results while Figures 10 and 11 report levelized costs.

- Figure 9 shows that the TCR varies from \$101/kW to \$78/kW. The results show that the cost of achieving an emission limit of 0.12 lb NO_x/MM Btu is about \$9.1/kW less when combustion controls are applied to reduce the boiler emission rate from 0.60 lb NO_x/MM Btu to 0.40 lb NO_x/MM Btu (Cases A and B).

- The effect of catalyst cost is also shown on Figure 9. Case C reflects a catalyst cost of \$330/ft^3 while Case A results reflect a cost of \$660/ft^3. The effect of the catalyst cost reduction is a \$23.2/kW (23%) drop in TCR.

- Figure 10 shows the cost components that make up the TCR for Coal Case A. The TPC makes up the largest component, of which the SCR Catalyst and Reactor cost component comprises approximately 60%.

- Figures 11 and 12 report the levelized cost of removing NO_x. Figure 11 shows that the lowest levelized SCR cost is for units with high uncontrolled NO_x emission rates. Comparison of the Case C and A results show that reduction in the catalyst cost from $660/ft^3 to $330/ft^3 would reduce the NO_x removal cost by $615/ton NO_x removed.

- Figure 12 shows that a catalyst cost reduction from $660/ft^3 reduces the LBC by about 1.5 mills/kWh (Case A vs C).

- Figure 13 shows the significance of expected catalyst life on LBC for both oil and coal. The expected catalyst life for the oil case is six years, while the expected life of the coal case is four years. These criteria show a dramatic decrease in the LBC when compared to previous results based on expected catalyst life of one to two years.

CONCLUSIONS

The conclusions developed in this study are:

1. The capital costs of retrofitting SCR to existing power plants in the U.S. are expected to be:

   A. $79 - 94/kW for oil-fired plants.
   B. $78 - 101/kW for tangentially-fired coal power plants.

2. The levelized costs of retrofitting SCR to existing power plants in the U.S. are expected to be:

   A. 3.5 to 12.2 mils/kWh for oil-fired plants
   B. 5.2 to 6.6 mils/kWh for tangentially-fired coal power plants.

3. The life cycle costs of SCR are driven primarily by capital costs for oil-fired units, particularly for retrofit applications. The life cycle costs of SCR for coal-fired units are equally effected by capital and operating/maintenance costs. This conclusion differs from past evaluations for new plants (EPRI CS-3603) in which high catalyst cost and a projected catalyst lifetime of one year led to operating costs dominating life cycle costs.

4. The installation of SCR NO_x control is expected to have an effect on the operation of downstream equipment including the air heater, I.D. fan, fly ash handling and disposal, ESP, FGD, and wastewater treatment system.

5. Unresolved technical issues in the application of SCR control to coal-fired power plants in the U.S. relate primarily to two issues:

   A. High sulfur coals - The conversion of SO_2 to SO_3, coupled with already high levels of SO_3 at the SCR inlet, can result in SO_3 concentrations of 40 ppm or higher at the SCR outlet. These high SO_3 levels could result in increased corrosion, air heater plugging, and plume opacity problems.

B. Coal trace elements - The trace elements in U.S coals are significantly higher, in many cases, than European or Japanese coals. These higher trace element concentrations may significantly reduce the catalyst life below the four years estimated in this study.

REFERENCES

1. Ando, J., "NO_x Abatement for Stationary Sources in Japan", EPA-600/7-79-205, August 1979.

2. Babcock & Wilcox, "Steam/Its Generation and Use", The Babcock & Wilcox Company, 1978.

3. Bauer, T.K., Spendle, R.G., "Selective Catalytic Reduction for Coal-Fired Power Plants: Feasibility and Economics", Stearns-Roger Inc., EPRI CS-3603, October 1984.

4. Brown and Caldwell, "Process Design Manual for Nitrogen Control", Environmental Protection Agency, EP 7.8/2:N59/975, October 1975.

5. Burke, J.M., Johnson, K.L., "Ammonium Sulfate and Bisulfate Formation in Air Preheaters", Radian Corporation, EPA-600/S7-82-025a, August 1982.

6. Cadrecha, M., "Preventing Acid Corrosion in Air Heaters", Power Engineering, January 1980.

7. Cichanowicz, J.E., Offen, G.P., "Applicability of European SCR Experience to U.S. Utility Operation", Proceedings: 1987 Joint Symposium on Stationary NO_x Control, EPA/EPRI, New Orleans, 1987.

8. Electric Power Research Institute (EPRI), TAG - Technical Assessment Guide, Volume I: Electricity Supply - 1986, EPRI P-4463-SR, December 1986.

9. Ellison, W., "Assessment of SO_2 and NO_x Emission Control Technology in Europe", EPA-600/2-88-013, February 1988.

10. Goldschmidt, K., "VKR Full-Scale SCR Experience on Hardcoal Fired Boilers", Proceedings: 1987 Joint Symposium on Stationary NO_x Control, EPA/EPRI, New Orleans, 1987.

11. Holcombe, L.J., Behrens, G.P. et al., "Manual for Management of Low Volume Wastes from Fossil-Fuel-Fired Power Plants", Radian Corp., EPRI CS-5281, July 1987.

12. Howard, G. et al., "Proposed Rule 1135 - Emissions of Nitrogen Oxides from Electric Power Generating Boilers", South Coast Air Quality Management District staff report, August 1988.

13. Itoh, H., Kajibata, Y., "Countermeasures for Problems in NO_x Removal Process for Coal-Fired Boilers", Proceedings of the Joint Symposium on Stationary Combustion NO_x Control, Volume II, October 1980.

14. Keeth, R.J., Balfour, D.A., "Utility Stack Opacity Troubleshooting Guidelines", EPRI RP 2250-3, Draft Report, January 1989.

15. Metcalf and Eddy, Inc., "Wastewater Engineering: Treatment, Disposal, Reuse", McGraw-Hill, 1979.

16. Nakabayashi, Y., Abe, R., "Current Status of SCR in Japan", Proceedings: 1987 Joint Symposium on Stationary NO_x Control, EPA/EPRI, New Orleans, 1987.

17. Necker, P., " Operating Experience with the SCR $DeNO_x$ Plant in Unit 5 of Altbach/Deizisau Power Station", Proceedings: 1987 Joint Symposium on Stationary NO_x Control, EPA/EPRI, New Orleans, 1987.

18. Osborn, H.H., "The Effect of Ammonia SCR $deNO_x$ Systems on Ljungstrom Air Preheaters", C-E Air Preheater, EPRI RP 835-2, June 1979.

19. Scheck, R.W., Damon, J.E., et al., "Technical and Economic Feasibility of Ammonia - Based Postcombustion NO_x Control", EPRI CS-2713, November 1982.

20. Scheck, R.W., Mora, R.R., Belba, V.H., Horney, F.A., "Economics of Fabric Filters and Electrostatic Precipitators - 1984", Stearns Catalytic Corporation, EPRI CS-4083, June 1985.

21. Singer, J.G., "Combustion: Fossil Power Systems", Combustion Engineering, Inc., 1981.

22. Swann, D.R., Drissel, G.D., "Feasibility of Retrofitting Catalytic Postcombustion NO_x Controls on an 80-MW Coal-Fired Utility Boiler", Stearns-Roger Incorporated, EPRI CS-1372, February 1980.

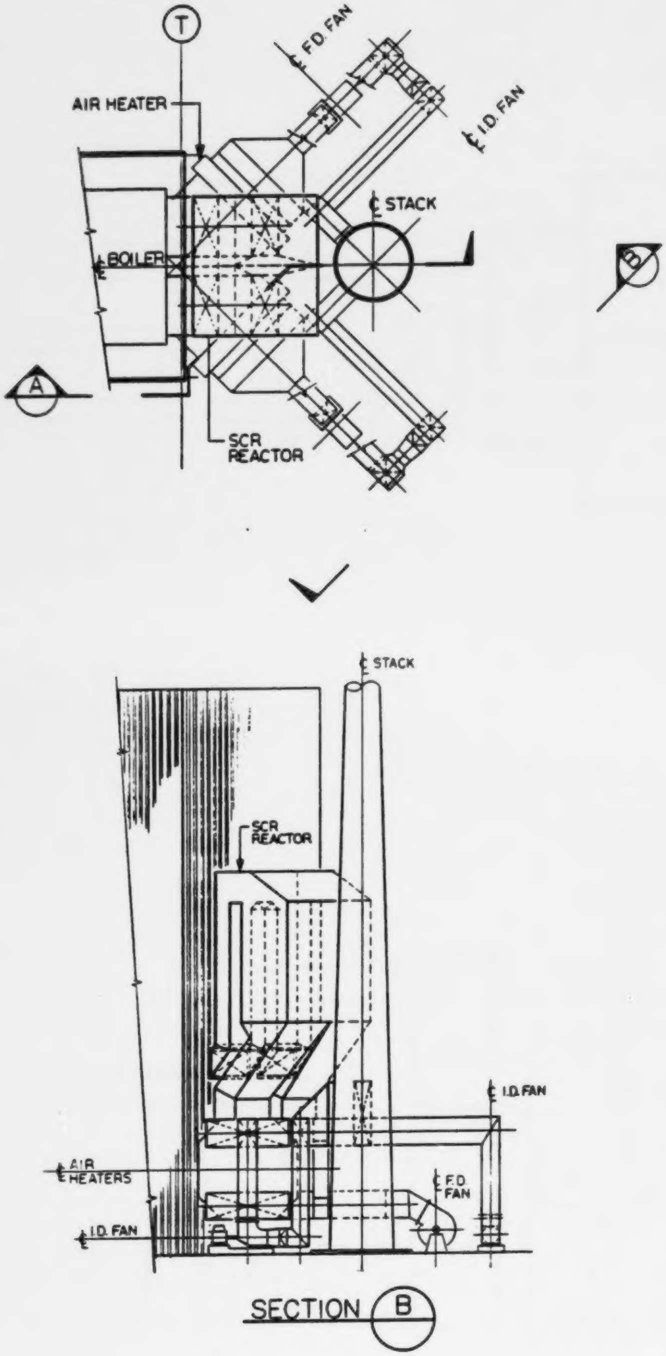


Figure 1. Oil Case: Plan and Elevation.

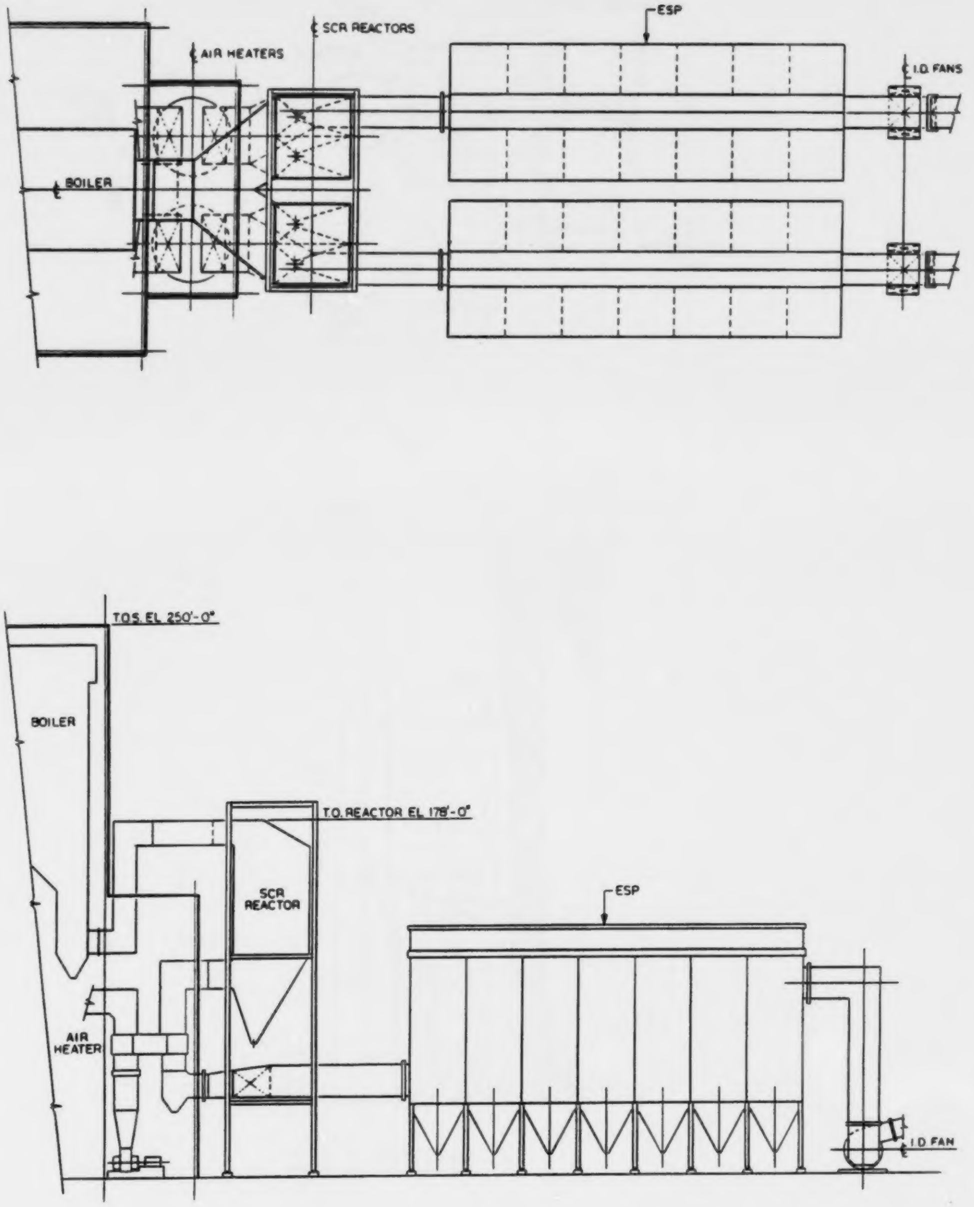


Figure 2. Coal Case: Plan and Elevation.

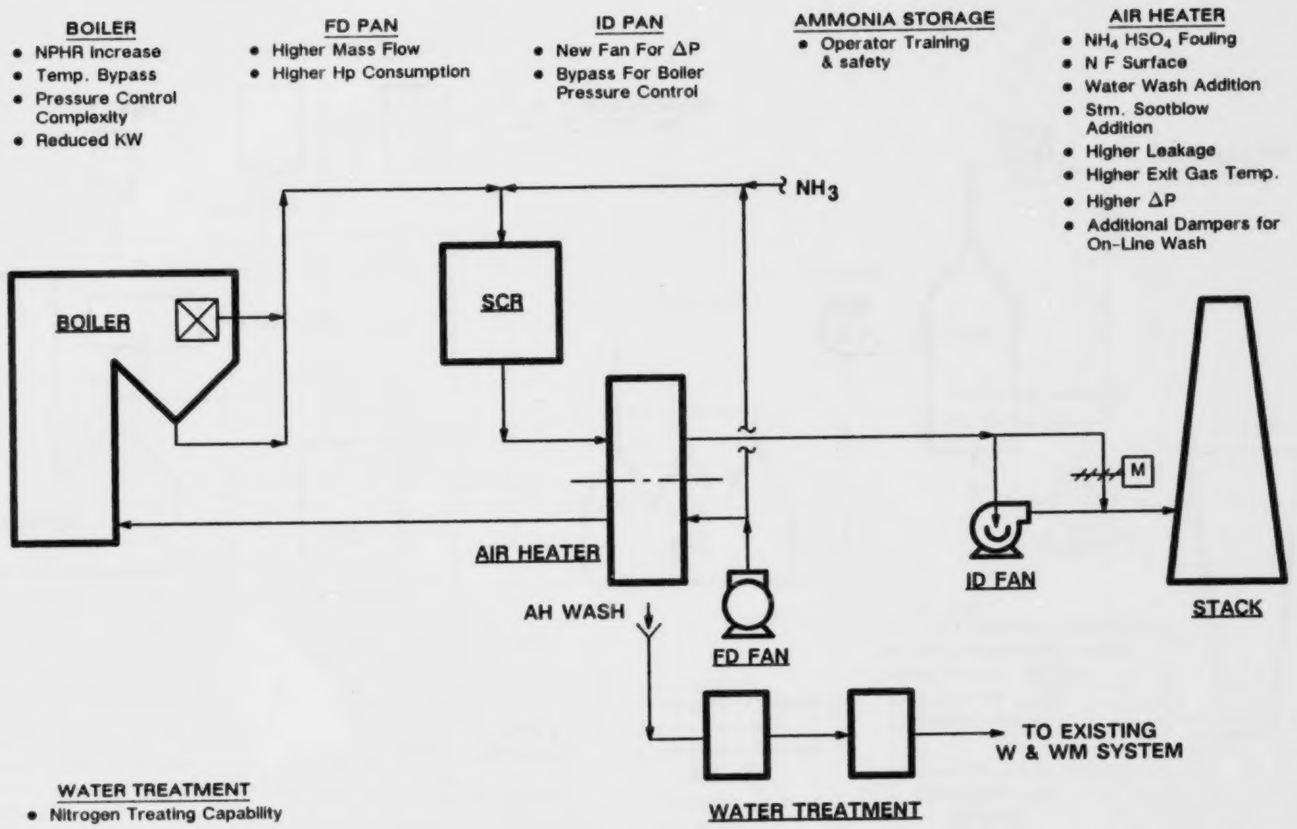


Figure 3. Oil Case: SCR Design/Operations Impact.

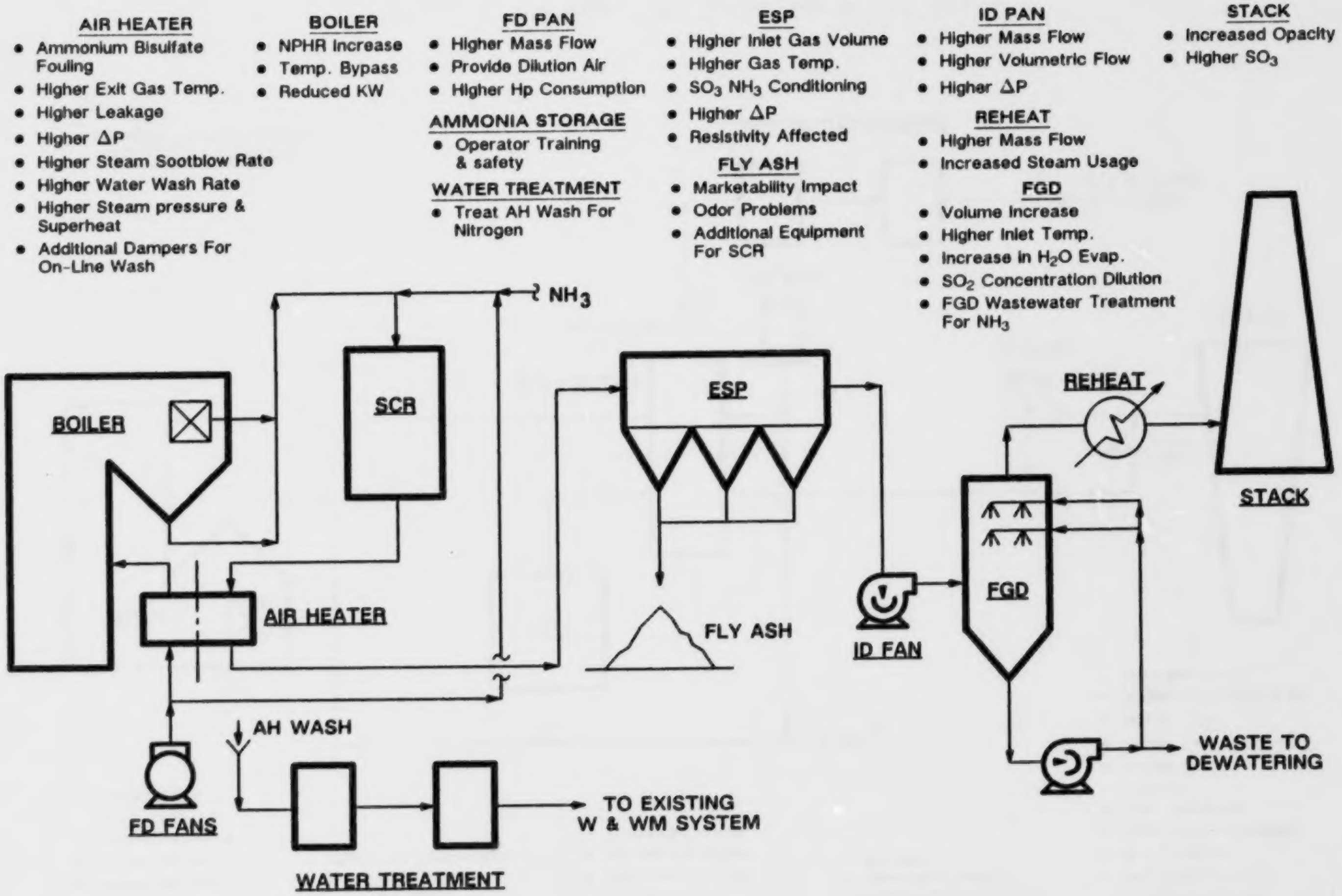
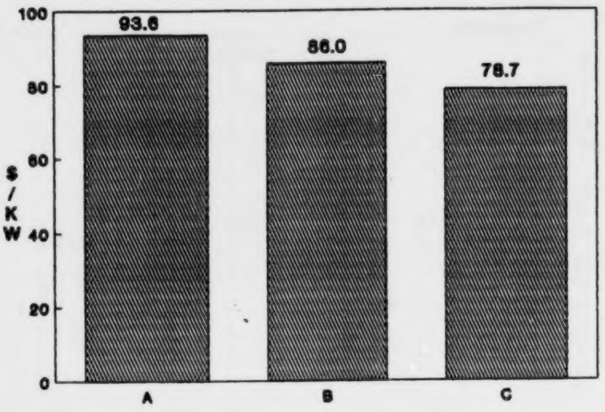


Figure 4. Coal Case: SCR Design/Operations Impact.



	A	B	C
CATALYST COST, $/FT^3	660	660	330
DENOX EFFICIENCY, %	90	80	90
BOILER OUT, #/MMBTU	0.30	0.15	0.30

Figure 5. Oil Case: Capital Cost Sensitivity, 1989 $.

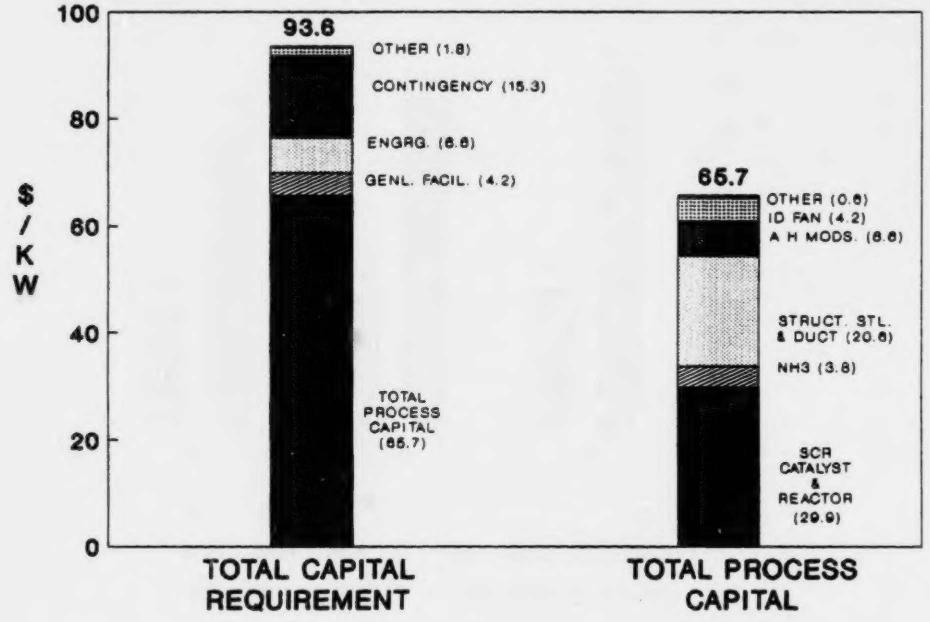
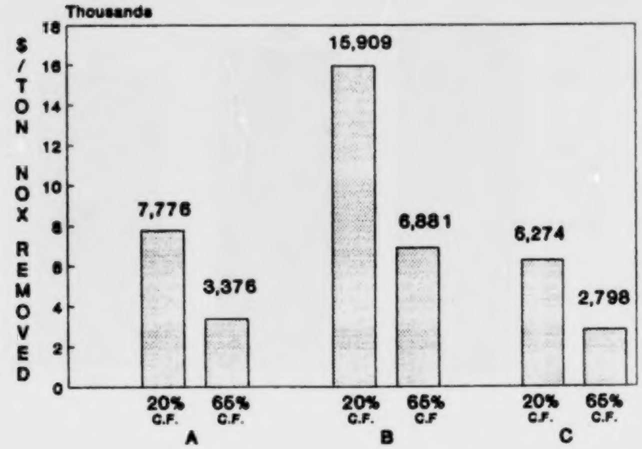
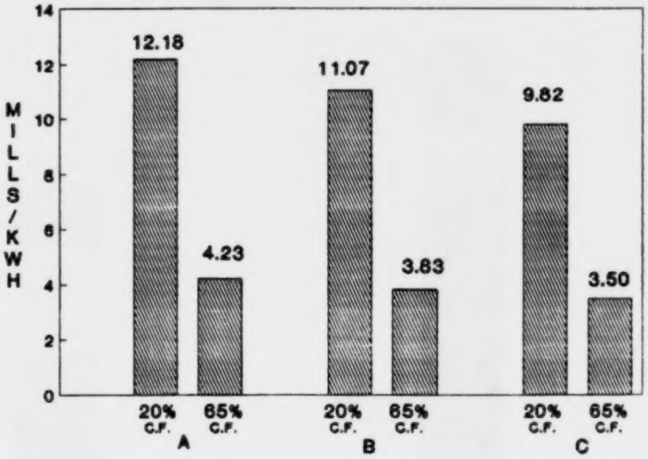


Figure 6. Oil Case A: Capital Cost of SCR, 1989 $.



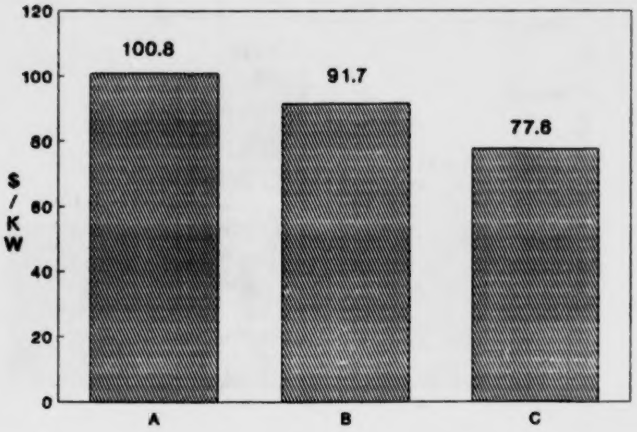
	A	B	C
CATALYST COST, $/FT^3	660	660	330
DENOX EFFICIENCY, %	90	80	90
BOILER OUT, LB/MMBTU	0.30	0.15	0.30

Figure 7. Oil Case: NO_x Removal Cost, Levelized 1989 $.



	A	B	C
CATALYST COST, $/FT^3	660	660	330
DENOX EFFICIENCY, %	90	80	90
BOILER OUT, #/MMBTU	0.30	0.15	0.30

Figure 8. Oil Case: Busbar Cost Sensitivity, Levelized 1989 $.



	A	B	C
CATALYST COST, $/FT^3	660	660	330
DENOX EFFICIENCY, %	80	70	80
BOILER OUT, #/MMBTU	0.60	0.40	0.60

Figure 9. Coal Case: Capital cost Sensitivity, 1989 $.

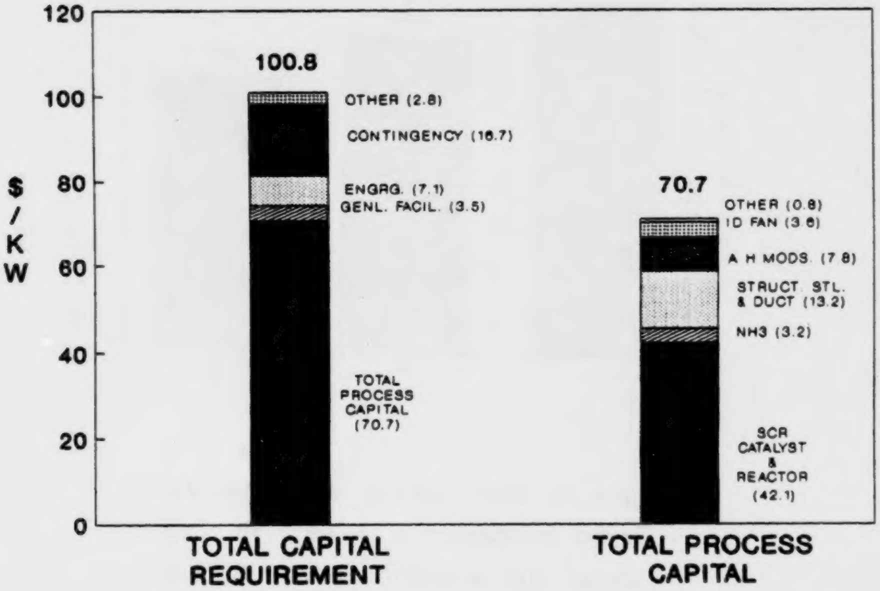
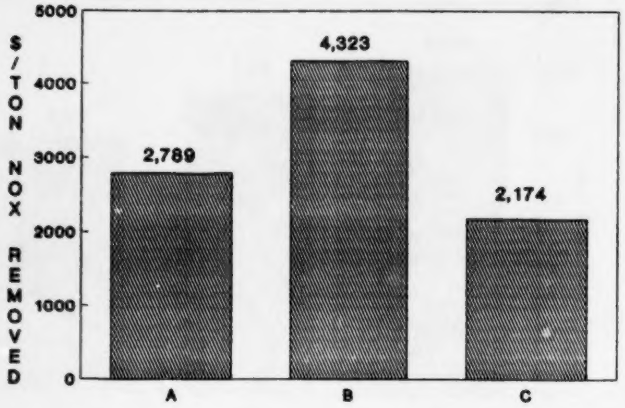
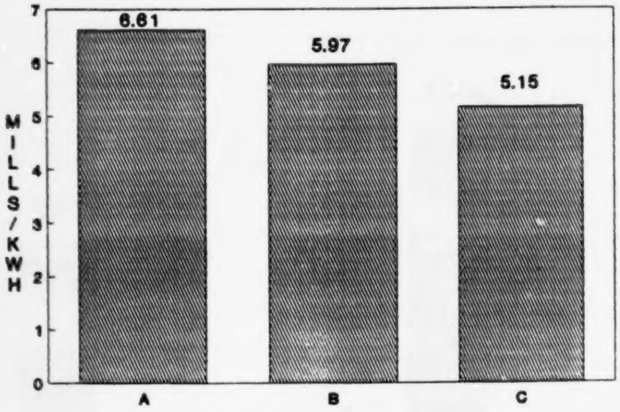


Figure 10. Coal Case A: Capital Cost of SCR, 1989 $.



	A	B	C
CATALYST COST, $/FT^3	660	660	330
DENOX EFFICIENCY, %	80	70	80
BOILER OUT, #/MMBTU	0.60	0.40	0.60
CAPACITY FACTOR, %	65	65	65

Figure 11. Coal Case: NO_x Removal Cost, Levelized 1989 $.



	A	B	C
CATALYST COST, $/FT^3	660	660	330
DENOX EFFICIENCY, %	80	70	80
BOILER OUT, #/MMBTU	0.60	0.40	0.60
CAPACITY FACTOR, %	65	65	65

Figure 12. Coal Case: Busbar Cost Sensitivity, Levelized 1989 $.

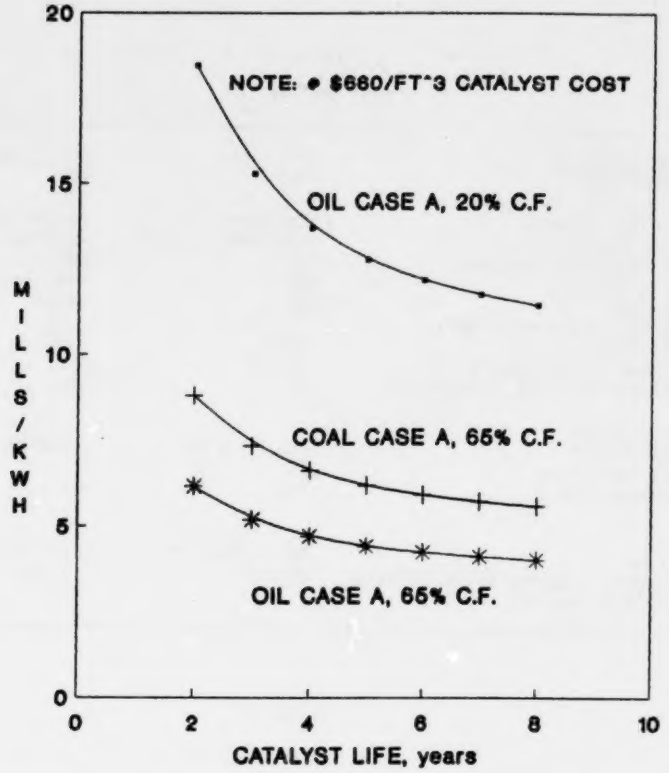


Figure 13. Busbar Cost vs. Catalyst Life, Levelized 1989 $.

Table 1

CASE DEFINITION

Plant Description	Oil Case	Coal Case
∘ Retrofit	Yes	Yes
∘ Capacity, MW (gross)	400	536
∘ Boiler Type	Pressure	Tangential
∘ Air Heaters	Horizontal, Twin	Vertical, Twin
∘ Particulate Control	No	ESP
∘ SO_2 Control	No	Wet Limestone
∘ Reheat	No	Steam
∘ Gross Plant Heat Rate, Btu/kWh	9004	9197
∘ Capacity Factor, %	20, 65	65
∘ Remaining Life, Years	20	20
Site Conditions		
∘ Location	Southern CA	Kenosha, WI
∘ Seismic Zone	IV	I
∘ Urban Site	Yes	No
Fuel		
∘ Type	No. 6 Fuel Oil	Bit. Appalachian
∘ Higher Heating Value, Btu/lb	18,814	13,100
∘ Sulfur Content, wt %	0.21	2.6

Table 2

SCR PROCESS DESIGN

	Oil Study Case		Coal Study Case	
	A	B	A	B
SCR Design Basis				
Economizer Outlet Temp. @ MCR, °F	654	654	725	725
Economizer Excess Air, %	12.5	12.5	24	24
Boiler NO_x Emission Rate, lb/MM Btu	0.30	0.15	0.60	0.40
NO_x concentration, ppmv (actual)	312	161	572	381
NO_x Emission Limit, lb/MM Btu	0.03	0.03	0.12	0.12
NO_x Reduction Rate, %	90	80	80	70
NH_3 Bleed Rate, ppmvd (@ 3% O_2)	10	10	5	5
Guaranteed Catalyst life, years	2	2	2	2
Reactor Configuration	Single, Vertical	Single, Vertical	Twin Vertical	Twin Vertical
Ammonia Storage, days	7	7	7	7
SCR Design				
Space velocity, SCF*/ft^3-hr	3370	3900	2500	2960
Linear Velocity, actual fps	21.0	21.0	18.2	18.2
Surface area, m^2/m^3	555	555	470	470
Pitch, mm	5.94	5.94	7.07	7.07
Catalyst layers (active + spare)	4 + 1	4 + 1	4 + 1	4 + 1
Soot Blowers	yes	yes	yes	yes
Ammonia Consumption, lb/hr	581	268	1,383	807
SCR Cost Development				
Catalyst Cost, $/$ft^3$	660	660	660	660
Expected Catalyst Life, years	6	6	4	4
Ammonia Cost, $/ton	145	145	145	145

*SCF at 32°F

Session 6B

FUNDAMENTAL COMBUSTION RESEARCH

Chairman: B. Martin, EPA

PREDICTION OF FUEL AND THERMAL NO IN ADVANCED COMBUSTION SYSTEMS

R.D. Boardman and L.D. Smoot
Department of Chemical Engineering
350 CB, Brigham Young University
Provo, Utah, 84604

ABSTRACT

A computer model to predict in-situ and effluent nitric oxide (NO) concentrations has been applied to advanced-concept, pulverized-coal systems and evaluated by comparing model predictions with experimental data. Specifically, the effects of pressure, stoichiometric ratio, air stage location, and temperature were predicted by the model and compared to experimental data. An overview of the model theory and its approach is presented. The basis for an expanded model including thermal NO and alternative fuel NO mechanisms to explore the capabilities of predicting low rank coal behavior and possibly fuel-staging (reburning) is discussed. This work is a continuation of previous model development and evaluations.[1,2]

INTRODUCTION

A significant effort has been made at modeling gaseous pollutants, including nitric oxides (NO_x). For instance, NO_x concentrations have been predicted for simple laboratory-burner hydrogen, carbon monoxide, and light hydrocarbon flames using well-defined mechanisms.[3,4,5] These approaches use scores of elementary reactions to calculate the pool of radical and stable oxy-hydroxyl, carbonaceous and nitrogenous species. Figure 1 shows a partially complete mechanism for the formation of NO from fuel nitrogen and illustrates the radical species involved in the rate equations. However, production of NO_x in practical combustion devices is significantly more complex and it would be extremely difficult to employ such a comprehensive mechanism, particularly for prediction of instantaneous radical species.

Consider a coal combustor in which nitrogen enters in the air and also as a fuel-bound constituent. It is essential to adequately predict the governing transport phenomena (*e.g.* fluid mechanics, heat transfer, and particle dispersion) and chemical kinetics involving both heterogeneous and homogeneous reactions. An adequate description of interactions between the chemistry and turbulent fluid mechanics also becomes imperative. Yet prediction of turbulent, coal-laden gas flow through swirling jets using the best closure models available is often insufficient. And even the most advanced devolatilization models which describe the combined physical and chemical processes are based on empirical correlations to macromolecular coal structure and laboratory measurement of mass evolution. For example, the FG/DVC (functional group/depolymerization-vaporization-cross-linking) coal devolatilization model by Solomon et al.[6] predicts species evolution and tar formation, employing rank-independent kinetic parameters, based on a number of general assumptions and coal pyrolysis observations. Hence, the ability to accurately predict the necessary spatially-dependent, instantaneous radical species, inherent in the complete kinetics mechanism, for turbulent coal flames is currently not possible.

Because it is almost always impossible to establish the exact reaction network which is universally applicable to all combustion configurations, it is desirable to reduce the nitrogen species chemistry to a subset of only the precursors, intermediates and products of greatest importance. The advantage of global kinetics, based on only key and measurable intermediates, is the ability to perform the calculations with greater efficiency and to account for the effects of turbulence. Also, a common level of sophistication between the coal conversion model and pollutant formation model is maintained.

A method for predicting the conversion of coal-bound nitrogen to NO was developed by Smith, Smoot, and Hill.[7,8] This same theory has also been adopted into other modeling codes.[9,10] This NO_x model is a component of a general combustion code that provides theoretical predictions for the temperature, velocity, major species, and other properties at local points throughout turbulent combusting flow fields. It assumes that a simplistic global kinetic model, explicit only in HCN, O_2, NO, and char surface area, is adequate to predict the formation and destruction of NO. Extensive evaluation of this model has been made and reported previously.[1,2,11] Although a promising degree of success has been demonstrated for this modelling approach, efforts to improve and to generalize the NO_x model for a larger variety of combustion applications are continuing.

MODEL DESCRIPTION AND THEORY

The strength of this approach to predict nitric oxide is that the model is coupled to a comprehensive combustion model, PCGC-2 ("Pulverized Coal Gasification and Combustion-2 dimensional"), applicable to both two-dimensional laboratory and industrial-scale practical combustors. PCGC-2 solves the set of general conservation equations for a gas/particle-laden reacting axi-symmetric system. Auxiliary equations are used to describe the chemical and physical processes while the two equation k-ε turbulence model is used.

Simulations provide predictions for the mean gas field properties and local particle properties for steady-state, turbulent flames. A brief description of the model is given here to give general insight into the comprehensive model.

The solution of the major field variables in PCGC-2 is based on the "fast" chemistry assumption where all gaseous reactions go to equilibrium locally, as soon as the reactants are released to the gas phase and mixed at a molecular level. Specification of the local pressure, enthalpy, and elemental composition is sufficient to determine the equilibrium composition, temperature, and fluid density of the gas mixture. For turbulent flames, it can be reasonably assumed that all species have equal turbulent diffusion coefficients. Thus, the local elemental composition is determined throughout the system by tracking the mixing of primary gas, secondary gas, and the coal offgas. Two conserved scalars, f (primary mixture fraction) and η (coal offgas mixture fraction), are used in PCGC-2 to track this mixing. The energy equation is then solved to determine the enthalpy. With knowledge of the instantaneous values of f, η, and enthalpy, the instantaneous values of species concentrations and temperature are uniquely determined. A detailed physical and mathematical description of the comprehensive model is given in a number of references.[12,37]

In the existing NO_x model theory of PCGC-2, fuel nitrogen release from coal is assumed to occur at a rate proportional to total coal weight loss. The volatile nitrogen is assumed to be instantaneously converted to HCN and is competitively reduced to N_2 by reaction of NO with HCN. The infinite kinetic rate assumption is no longer invoked. In fact, random fluctuations in the temperature and species composition dramatically influence the mean reaction rates. A method for obtaining mean reaction rates from information provided by the progress variables is possible, provided the instantaneous temperature and species concentrations are unique functions of the instantaneous progress variables. While PCGC-2 does not solve directly for the instantaneous values of the progress variables, a statistical distribution of the instantaneous values about the mean can be hypothesized. Given the mean value of the progress variable (first moment), its variance about the mean (second moment) and an assumed shape (called a probability density function - pdf) for its distribution, the values of the instantaneous properties can be statistically determined. Both the first and second moments are provided by the turbulence model. Experimental and modeling experience has provided information for choosing the shape of the probability density function. Typically, a clipped Gaussian distribution with intermittency for pure primary and pure secondary air is selected for the pdf. The mean rates are thus obtained by integrating the instantaneous rates over the statistical probability of the progress variables. When two progress variables are involved, the integration is made over a double integral which expresses the joint probability of each progress variable. The overall mechanism is shown in Figure 2 and key model equations are listed in Table I.

PREDICTIONS IN ADVANCED COMBUSTION SYSTEMS

Initial evaluation of the NO_x model has demonstrated the ability of the model to predict the effects of increasing stoichiometric ratio (S.R.) for both swirling and non-swirling diffusion flames in single-stage, laboratory-scale and pilot-plant combustors.[2] Experimental NO data passed through a minimum at a swirl number of 2.0 - 3.0, depending on the coal type. At a S.R. of 1.0, the model was also shown to reliably predict the effects of particle size on NO emissions and also the trend of increasing NO concentrations with increasing coal moisture content.[1]

In order to further investigate the utility of the NO_x model, application and evaluation has been made for advanced-concept, coal-combustion systems of entrained-flow gasification, fuel-rich and staged combustion, and CO2-O2 oxidizer combustion. Specifically, the effects of pressure, stoichiometric ratio, air stage location, and temperature were predicted by the model and compared to experimental data. Experimental data sources for model comparisons were selected for axi-symmetric combustion experiments where systematic variation of key test variables (*e.g.*, pressure or S.R.) were reported. Table II lists the combustion configurations, reactor dimensions, coal types, firing rates, and other parameters. Comparisons of predicted NO concentrations with experimental measurements were made after acceptable agreement for the main stream variables was demonstrated.[13]

NON-STAGED, AIR-COAL COMBUSTION

Cases were simulated for non-staged combustion at fuel-lean (S.R. = 1.20), near stoichiometric ratio (S.R. = 0.95) and moderately fuel-rich (S.R. = 0.80) conditions. Figure 3 compares the theoretical and experimental effluent NO concentrations over the range of stoichiometric ratios shown. The measured data and axial profiles are compared in Figure 4 for each case. For the fuel-lean case, a high peak NO concentration is predicted initially but the profile rapidly decays to approximately 8 percent above the experimental profile. A similar trend is predicted for S.R. = 0.95, except that the NO profile decays to a level 10-15 percent below the measured data. The predicted NO concentrations also follow this trend for the SR = 0.80 case but are consistently lower by 15 to 30 percent along the entire profile. The discrepancies between the measured and predicted NO concentrations in the early region of the reactor may be due to non-isokinetic sampling. The reactor was designed to establish one-dimensional flow;[14] however, it is possible that radial stratification of the flame occurred in the vicinity of the burner.

In fact, the NO concentration profile predicted near the wall closely matched the experimental data throughout the entire reactor, including the early region. A separate explanation for this discrepancy may be a result of assuming that fuel nitrogen is evolved at a rate proportional to the total coal mass loss. Wendt[15] found that at low temperature, the early volatiles are nitrogen-free. If the rate of nitrogen release is lower than the total coal mass loss, then the model could overpredict the formation of NO in the near-burner region.

AIR STAGED COMBUSTION

Staged combustion cases were accomplished by injecting additional air downstream of the fuel-rich primary zones. Two simulations each were completed for primary zone S.R. values of 0.95 and 0.80 respectively. The secondary-zone air was injected into the reactor at axial locations corresponding to residence times of 0.52 s and 0.90 s, bringing the overall reactor S.R. to 1.20. Experimentally, it was demonstrated that secondary-stage NO concentrations were independent of primary zone NO levels[14]; however, effluent NO concentrations were decreased as the first stage was lengthened because of the fast rate of NO decline in the fuel-rich, high-temperature, primary zone. Figure 5 shows the incremental reduction in NO at the exit for both primary-zone stoichiometric ratios. A difference of ~200 ppm NO was measured between the secondary-air stage locations of 0.52 s and 0.90 s for each case. The predicted difference in NO concentration at the exit closely matches the measured trend.

TEMPERATURE DEPENDENCE

The effects of temperature on fuel NO have been elucidated in a number of investigations. From data of fuel-lean (15% excess oxygen) pulverized-coal diffusion flames, fuel NO was observed to be essentially constant over a temperature range up to 2550 K for four coal types.[16] One of the coal types investigated was Colorado bituminous coal. Model simulations have also been made for Colorado bituminous coal, in a separate reactor but at similar operating conditions using nitrogen substituted carrier gas at 15% excess oxygen. A similar temperature insensitivity is shown in Figure 6 for the model predictions which closely follows the trend measured by Pershing and Wendt.[16]

ROLE OF HETEROGENEOUS DECAY

Predictions were examined to determine the relative difference between homogeneous and heterogeneous NO reduction. In most fuel-rich locations, where concentrations of HCN were appreciable, the heterogeneous decay was found to be insignificant compared to the magnitude of homogeneous NO decay. This result is consistent with the experimental observation[17] that gas-phase destruction of NO is the dominant NO reduction path in fuel-rich coal combustion. Homogeneous decay was far more significant for the gasifier predictions because of the high concentration of fuel-rich species. However, for the non-staged combustion cases, homogeneous decay was only initially more significant but became relatively less important as the fuel-rich species were consumed. Thus, in the aft section of the combustor, heterogeneous NO decay also became important.

ENTRAINED-FLOW GASIFICATION

Four simulations of three coal types were completed. Figures 7 and 8, respectively, compare the experimental and theoretical NO concentration profiles for atmospheric and high pressure (5 atm) gasification of Utah bituminous coal. Predicted and measured peak NO concentrations are similar in magnitude and location. Predicted concentration contours closely match the experimental maps for the atmospheric case throughout the entire reactor while the high pressure case also matches the peak NO value but decays somewhat slower. A predicted exit concentration of 100 ppm is approximately 30 percent below the measured value for the atmospheric pressure case while the predicted exit value of 4 ppm differs by only two ppm from the measured value for the high pressure case.

Results for the simulation of Illinois bituminous coal were similar to the Utah bituminous coal. However, for North Dakota lignite, although the major species and flame structure were predicted adequately, Figure 9 shows that both the location and magnitude of peak NO concentration were incorrectly predicted. Instead, the predictions resemble those of the bituminous coals. It has been observed that lignites, relative to bituminous coals, produce larger quantities of NH_3 during gasification.[18] It was also observed in this study that NH_3 concentration measurements for the North Dakota Lignite were 200-300 percent higher than for the Utah and Illinois bituminous coals. Evidence suggests that the initial release of NH_3 and HCN provide an estimate of the amount of nitrogen reduction occurring in the vicinity of the reacting particles.[19] Available data suggest that the gas-phase fuel-nitrogen reaction sequence is initiated by a rapid and nearly quantitative conversion of the parent fuel nitrogen compounds to hydrogen cyanide and ammonia. HCN appears to be the principal product when the fuel nitrogen is bound in a aromatic ring while NH_3 is the principal product when the fuel nitrogen is bound with amines.[20] As coal rank decreases, the number of rings also decreases and hence the conversion of fuel nitrogen to NH_3 rather than HCN. Additionally, the rate of nitrogen release from lignite coal likely does not occur at a rate proportional to total coal mass loss. Since the existing NO model mechanism considers only HCN, NO, and O_2 species, the inclusion of NH_3 in the global rate expressions as well as an advanced devolatilization model to predict nitrogen species devolatilization may improve the model for low rank coals simulations.

MODEL IMPROVEMENTS

From comparisons of model predictions to a diversity of experimental data, a number of potential improvements to the NO_x submodel have been identified. It is recognized that the simplified mechanism will not adequately account for the recycle of NO and HCN via reaction with hydrocarbons and nitrogen intermediates as postulated by Bartok and Folsom[21] and Kramlich et al.[19] Second, since possible explanations for the discrepancies noted above for the prediction of lignite coal gasification suggest the importance of intermediate species NH_i, a more complete global fuel-NO mechanism is being sought. Finally, the incorporation of thermal NO would further improve the usefulness of model for predicting gas and fuel-oil practical combustors. Improvements to the major combustion code, PCGC-2, and the devolatilization model are being sought as part of ongoing efforts to develop generalized combustion simulators.[22]

JOINT FUEL AND THERMAL NO MODEL

Recent modifications to the theory have included the addition of the extended Zeldovich mechanism to the NO_x model. Simplifying options have been included in the code to allow investigation of techniques to predict radical oxygen which appears in the rate equation. Radical O will be estimated by assuming partial equilibrium relationships among pertinent species according to the method demonstrated by Sarofim and Pohl[23]. With provisions for thermal NO formation incorporated in the model it is possible to predict the joint formation of fuel and thermal NO. Figure 10 shows a comparison of a model prediction with experimental data for gasification of Utah bituminous coal. Joint prediction of fuel and thermal NO increased the peak centerline NO concentration by 25 percent over the value predicted by fuel NO alone. And, although the predictions do not fit every datum well, it is clear that the addition of thermal NO to the theory improved the model prediction throughout the entire profile.

A study is planned to measure thermal NO in a turbulent gaseous flame reactor with heating rates equivalent to industrial combustors. This effort should provide useful information for selecting suitable partial equilibrium assumptions when predicting radical oxygen concentrations.

ALTERNATIVE FUEL NO MECHANISM

Although a promising degree of success has been demonstrated with the fuel NO mechanism postulated by Smith et al.[7], for predicting formation and destruction of NO in bituminous coal flames over diverse conditions, predictions for low-rank coals have often lacked good quantitative agreement as demonstrated earlier. One explanation for this has been suggested to be the exclusion of NH_3 as a species in the global model of Figure 2. A review of NO_x mechanism investigations has been made with the purpose of identifying possible alternative global fuel-NO mechanisms which include NH_3 in the correlated rate equations.

Fenimore[24-28], measured traverses of HCN, NH_3, and NO throughout the burnt gas of fuel-rich gaseous flames and postulated decay reactions for each species. According to this mechanism, HCN and NO are destroyed by the sequence:

$$\mathbf{HCN} + OH \rightarrow NH_3 + \text{products} \qquad (1)$$

$$NH_2 + \mathbf{NO} \rightarrow N_2 + H_2O \qquad (2)$$

These global rates apply specifically to the decay of nitrogenous species but do not account for either the formation of NO or HCN. Investigators have applied the Fenimore reactions to coal systems to determine better rate parameters.[17,29-31] In a study of fuel-rich combustion of pulverized coal, Dannecker and Wendt (1984) determined that although there is some variation from coal to coal, their data support the hypothesis that N_2 and NH_3 formation and NO destruction follow the Fenimore mechanism. The destruction of NO appeared to be approximately first order which was consistent with Fenimore's mechanism only if NH_2 is constant and can be predicted.

Although variations of Fenimore kinetics are useful for predicting the decay of NH_3 and NO in the post-flame region, it is also necessary to predict the formation rates of these species. From the literature, two simplified mechanisms involving NH_3 were identified that could be potentially adapted to the existing NO_x model. The first mechanism is the reaction sequence shown in Figure 11 postulated by Miller et al.[32] and includes the dominant reactions of those shown in Figure 1 for converting HCN to NO and N_2. This simplified mechanism was determined by performing sensitivity and rate-of-production analysis to match experimental data. Favorable results have been shown for a one-dimensional, premixed, laminar flame, a perfectly stirred reactor, and the time history of a homogeneous reaction.[3] Although this mechanism is based on well-established elementary rate with known kinetic parameters, unfortunately, even this simplified mechanism requires the predictions of radical species H, O, and OH. Currently, it has not been shown possible to calculate these radicals *a priori* in turbulent coal flames.

A global model has been presented by Mitchell and Tarbell[33] involving NH_3, HCN, NO, and N_2 as active centers. Figure 12 shows the global mechanism formulated by Mitchell and Tarbell. By assuming the form of the rate equations, which included formation of thermal NO assuming partial equilibrium of radical oxygen with molecular oxygen, Mitchell and Tarbell calculated the "best-fit" of relevant data to obtain the kinetic parameters for fuel NO formation and destruction. Extensive data of Muzio *et al.*,[34] covering a broad range of temperatures and ammonia-NO stoichiometries in CH_4/excess-air flames in a plug flow reactor were correlated to rate equations having the global form:

$$NH_3 + O_2 \rightarrow NO + H_2O + 1/2H_2 \qquad (3)$$

$$NH_3 + NO \rightarrow N_2 + H_2O + 1/2H_2 \qquad (4)$$

Since the rates were not each established through separate, independent measurements, the applicability of the mechanism remains questionable. It was determined to investigate the feasibility of this alternative mechanism by comparing it to predictions of the existing fuel NO mechanism of Hill, Smoot, and Smith.[1] Table III compares the two fuel NO mechanisms and lists specific advantages and disadvantages of each. A program scheme has been developed to allow the option of selecting between the fuel NO mechanism of Smoot, Smith, and Hill (References) and that of Mitchell and Tarbell. Presently, simulations are being made to investigate the later model. Although it does provide a path for the recycle of NO back to HCN, it is still not considered to be completely sufficient for predicting fuel-staging applications. It does include thermal NO contributions assuming the extended Zeldovich mechanism with radical oxygen in partial equilibrium with molecular oxygen only.

Figure 13 summarizes the revised NO model which has been expanded to include rates of thermal NO formation and an optional fuel NO mechanism which is currently being investigated. The relationship to the generalized combustion code is illustrated.

SUMMARY

Given the complexity of chemical reactions in practical, turbulent coal flames, it is difficult to apply comprehensive kinetic mechanisms, involving undeterminable trace and radical intermediates, to predict the formation and destruction of NO in a manner universally applicable to combustion configurations. Hence a global fuel NO mechanism has been used to predict NO concentrations in pulverized coal flames. Simulation results have shown favorable agreement with experimental measurements for a variety of combustion configurations for bituminous and sub-bituminous coals. With the exception of low rank coals and reburning configurations, the model may be used to predict NO emissions and to investigate the impact of changes in operating variables such as stoichiometric ratio, burner swirl number, reactor pressure, and air staging. Efforts are being made to further generalize the code by including the extended Zeldovich mechanism to predict thermal NO formation and an expanded global fuel NO mechanism into the code. The goal is to provide a model that can be used to aid in optimizing NO_x control strategies.

ACKNOWLEDGEMENTS

This work is supported by Morgantown Energy Technology Center (Contract No. DE-AC21-86MC23075 under subcontract from the Advanced Fuel Research, Co. Financial support for the model evaluation came from a Consortium of eleven organizations (Advanced Fuel Research, Babcock & Wilcox, Combustion Engineering, Consolidation Coal Co., Electric Power and Research Institute, Empire State Electric Energy Research Co., Foster Wheeler, Tennessee Valley Authority, U.S. DOE/METC, U.S. DOE/PETC, Utah Power & Light).

REFERENCES

1. Hill, S.C., L.D. Smoot, and P.J. Smith, Prediction of Nitrogen Oxide Formation in Turbulent Coal Flames," *Twentieth Symposium (International) on Combustion*, The Combustion Institute, Pittsburgh, PA, 1391 (1984).

2. Smith, P.J., L.D. Smoot, and S.C. Hill, "Effects of Swirling Flow on Nitrogen Oxide Concentration in Pulverized Coal Combustors," *AIChE Journal*, 1917 (1986).

3. Miller, J.A., and Bowman, C.T., "Mechanism and Modeling of Nitrogen Chemistry in Combustion," Western States Section/Combustion Institute, Dana Point, CA (1988).

4. Peck, R.E., P. Glarborg, and J.E. Johnsson, "Kinetic Modeling of Nitrogen Oxide Formation in Coal-Dust/Oxidizer Flat Flames,"Western States Section/Combustion Institute, Honolulu, HA (1987).

5. Glarborg, P., J.A. Miller, and R.J. Kee, "Kinetic Modeling and Sensitivity Analysis of Nitgrogen Oxide Formation in Well-Stirred Reactors," *Combustion and Flame*, **65**, 177 (1986).

6. Solomon, P.R., Hamblen, D.G.., Carangelo, R.M., Serio, M.A., and Deshpande, G.V., "General Model of Coal Devolatilization," *Energy & Fuels*, **2**, 405, (1988).

7. Smith, P.J., and S.C. Hill, and L.D. Smoot, "Theory for NO Formation in Turbulent Coal Flames," *Nineteenth Symposium (International) on Combustion*, The Combustion Institute, Pittsburgh, PA, 1263 (1982).

8. Hill, S.C., "Modeling of Nitrogen Pollutants In Turbulent Pulverized-Coal Flames," Ph.D. Dissertation, Department of Chemical Engineering, Brigham Young University, Provo, UT (1983).

9. Zinser, W. and U. Schnell, "Application of Mathematical Flame Modelling to NO_x Emissions from Coal Flames," Fundamentals of Physical Chemistry of Pulverized Coal: J.Lahaye edt., NATO ASI Series, Martinus Nijhoff Publishers (1987).

10. Fiveland, W.A. and Wessel, R.A., "Numerical Model for Predicting the Performance of Three Dimensional Fuel Fired Furnace," *Eng. for Gas Turbines and Power*, **110**, No. 1, 117, (1988).

11. Boardman, R.B. and L.D. Smoot, "Prediction of Nitric Oxide in Advanced Combustion Systems, "*AIChE Journal*, **34**, No.9, 1573, (1988).

12. Smoot, L.D. and P.J. Smith, Coal Combustion and Gasification, Plenum Press, New York, NY (1985).

13. Boardman, R.D., "Further Evaluation of a Predictive Model for Nitric Oxide Formation During Pulverized Coal Combustion," Master's Thesis, Brigham Young University, Provo, UT (1987).

14. Wendt, J.O.L, J.W. Lee, and D.W. Pershing, "Pollutant Control Through Staged Combustion of Pulverized Coal," U.S.Department of Energy Technical Progress Report for Period January 1977 - December 1977, FE-1817-4, (1978).

15. Wendt, J.O.L.,"Fundamental Coal Combustion Mechanisms and Pollutant Formation in Furnaces," *Prog. Energy Combustion Sci.*, **6**, 201 (1980).

16. Pershing, D.W. and J.O.L. Wendt, "Pulverized Coal Combustion: The Influence of Flame Temperature and Coal Composition on Thermal and Fuel NO_x" *Sixteenth Symposium (International on Combustion,* The Combustion Institute, Pittsburgh, PA, 389 (1977).

17. Dannecker, K.M. and J.O.L. Wendt, "Fuel Nitrogen Mechanism During the Fuel Rich Combustion of Pulverized Coal," paper 119c presented at the AIChE Annual Meeting, San Francisco, CA (1984).

18. Freihaut, J.D., W.M. Proscia, and D.J. Seery, "Fuel Bound Nitrogen Evolution During the Devolatilization and Pyrolysis of Coals of Varying Rank," *1987 Joint Symposium on Stationary Combustion NOx Control*, New Orleans, LA, March 23 - 26 (1987).

19. Kramlich, J.C., Lester, T.W. and Wendt, J.O.L., "Mechanisms of Fixed Nitrogen Reduction in Pulverized Coal Flames,"*1987 Joint Symposium on Stationary Combustion NOx Control*, New Orleans, LA, March 23 - 26 (1987).

20. Axworthy, A.E. and Dayan, V.H., "Chemical Reaction in the Conversion of Fuel Nitrogen to NO_x: Fuel Pyrolysis Studies," *Second EPA Stationary Source Combustion Symposium*, Sept., (1977).

21. Bartok, W. and Folsom, B.A., "Gas Reburning-Sorbent Injection - A Combined NO_x/SO_x Control Technology,"*1987 Joint Symposium on Stationary Combustion NOx Control*, New Orleans, LA, March 23 - 26 (1987).

22. Solomon, P.R., Serio, M.A., Hamblen, D.G., Smoot, L.D., and Brewster, B.S., "Measurement and Modeling of Advanced Coal Conversion Processes," 2nd Annual Report, D.O.E./M.T.C.E. contract DE-AC21-86MC23075, (Sept, 1988).

23. Sarofim, A.F., and J.H. Pohl, "Kinetics of Nitric Oxide Formation in Premixed Laminar Flames, "*Fourteenth Symposium (International) on Combustion*, The Combustion Institute, Pittsburgh, PA, 739 (1973).

24. Fenimore, C.P., "Studies of Fuel-Nitrogen Species in Rich Flame Gases," *Seventeenth Symposium (International) on Combustion*, The Combustion Institute, Pittsburgh, PA, 661 (1979).

25. Fenimore, C.P., "Reactions of Fuel-Nitrogen in Rich Flame Gases," *Combust. and Flame*, 26, 249 (1976).

26. Fenimore, C.P., "Formation of Nitric Oxide from Fuel Nitrogen in Ethylene Flames," *Combust. and Flame*, **19**, 289, October, (1972).

27. Fenimore, C.P., "Formation of Nitric Oxide in Pre-mixed Hydrocarbon Flames," *Thirteenth Symposium (International) on Combustion*, The Combustion Institute, Pittsburgh, PA, 373 (1971).

28. Fenimore, C.P. and H.A. Fraenkel, "Formation and Interconversion of Fixed Nitrogen Species in Laminar Diffusion Flames," *Eighteenth Symposium (International) on Combustion*, The Combustion Institute, Pittsburgh, PA, 143 (1981).

29. Glass, J.W. and J.O.L. Wendt, "Mechanisms Governing the Destruction of Nitrogenous Species During the Fuel Rich Combustion of Pulverized-Coal," Western States Section/Combustion Institute, University of Utah, Salt Lake City, UT (1982).

30. Bose, A.C., K.M. Dannecker, and J.O.L. Wendt, "Coal Compostition Effects on Mechanisms Governing the Destruction of NO and Other Nitrogenous Species during Fuel-Rich Combustion," *Energy and Fuels*, **2**, 301 (1988).

31. Bose, A.C. and J.O.L. Wendt, "Effect of Coal Compostition on Mechanisms Governing the Destruction of Nitrogenous Species During Staged Combustion," Western States Section/Combustion Institute, Honolulu, HA (1987).

32. Miller, J.A., M.C. Branch, W.J. McLean, D.W. Chandler, M.D. Smooke, and R.J. Kee, "The Conversion of HCN to NO and N_2 in H_2-O_2-HCN-Ar Flames at Low Pressure,"*Twentieth Symposium (International) on Combustion*, The Combustion Institute, Pittsburgh, PA, 673 (1984).

33. Mitchell, J.W., and J.M. Tarbell, "A Kinetic Model of Nitric Oxide Formation During Pulverized Coal Combustion," *AIChE Journal*, **28**, 302 (1982).

34. Muzio, L.J., J.K. Arand, and D.P. Teixeira, "Gas Phase Decompostion of Nitric Oxide in Combustion Products," *Sixteenth Symposium (International) on Combustion*, The Combustion Institute, Pittsburgh, PA, 199 (1977).

35. de Soëte, G.G., "Overall Reaction Rates of NO and N_2 from Fuel Nitrogen," *15th (International) on Combustion*, The Combustion Institute, Pittsburgh, PA, 1093 (1975).

36. Zeldovich, Y.B., P.Y. Sadovnikov, and D.A. Frank-Kamentskii, "Oxidation of Nitrogen in Combustion" (translated by Shelef), *Academy of Sciences of USSR* (1947).

37. Smoot, L.D., "Modeling of Coal-Combustion Processes," *Prog. Energy Combust. Sci.*, **10**, 229 (1984).

38. Levy L.M., Chan, L.K., Sarofim, A.F., and Beèr, J.M., "NO/Char Reactions at Pulverized Coal Flame Conditions," *Twentieth Symposium (International) on Combustion*, The Combustion Institute, Pittsburgh, PA, 111 (1981).

39. Brown, B.W., "Effects of Coal Type on Entrained Gasification," Ph.D. Dissertaion, Brigham Young University, Provo, UT (1985).

40. Nichols, K.M., Hedman, P.O., and Smoot, L.D., "Release and Reactions of Fuel-Nitrogen in a High-Pressure Entrained-Coal Gasifier," *Fuel*, **66**, 1257 (1987).

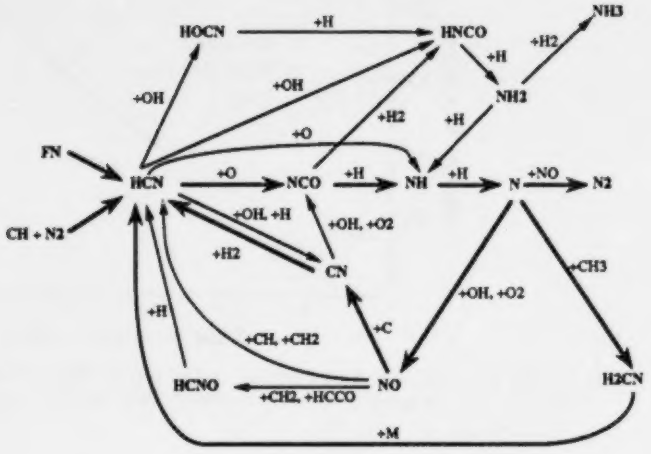


Figure 1. Partially complete mechanism for conversion of fuel NO to NO and N_2. (Source: Miller and Bowman[3])

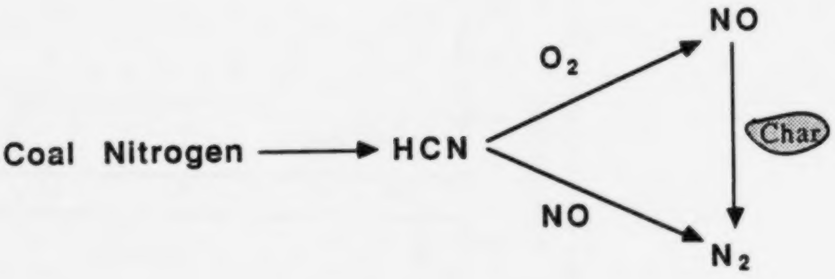


Figure 2. Global fuel NO mechanism of Hill, Smith, and Smoot,[1,2] using homogeneous rate expressions measured by de Soëte,[35] and char reduction rate expression measured by Levy et al.[38]

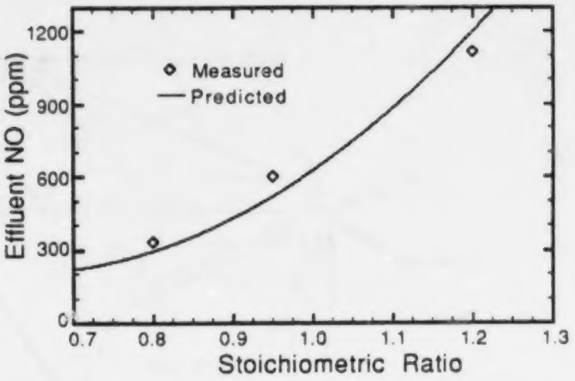


Figure 3. Comparison of predicted effluent NO concentrations for various reactor stoichiometries with experimental data of Wendt et al.[14]

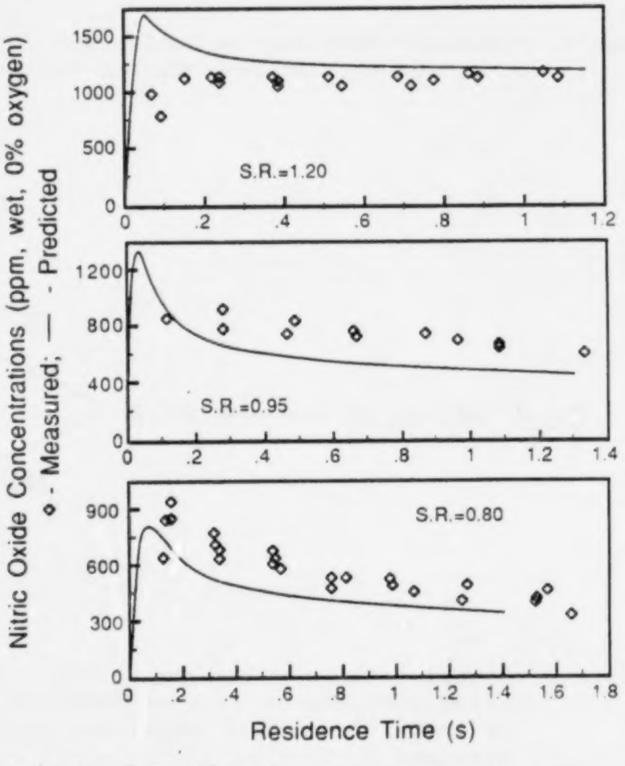


Figure 4. Comparison of predicted centerline NO profiles with experimental data of Wendt et al.[14]

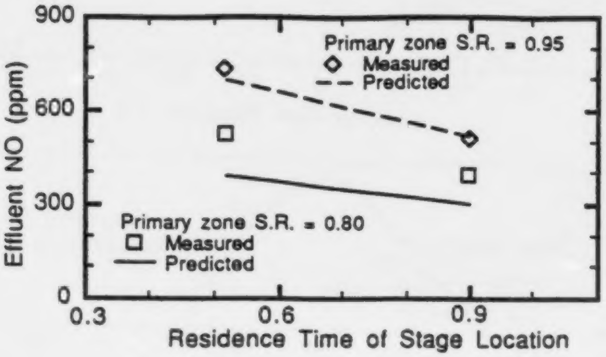


Figure 5. Comparison of predicted effluent NO concentrations for air-staged combustion with measured data of Wendt et al.[14] Secondary air injection located downstream from the primary burner at axial positions corresponding to residence times of either 0.52 sec. or 0.90 sec.

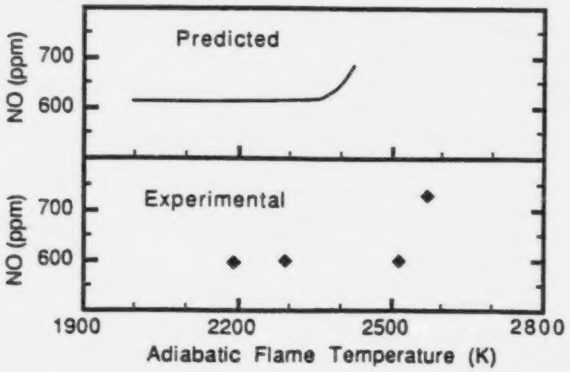


Figure 6. Temperature insensitivity of effluent NO concentrations for fuel-lean combustion of Colorado bituminous coal in CO_2-O_2 oxidizer. Measured data are from Pershing and Wendt[16]. Test conditions for measured and predicted cases differed.

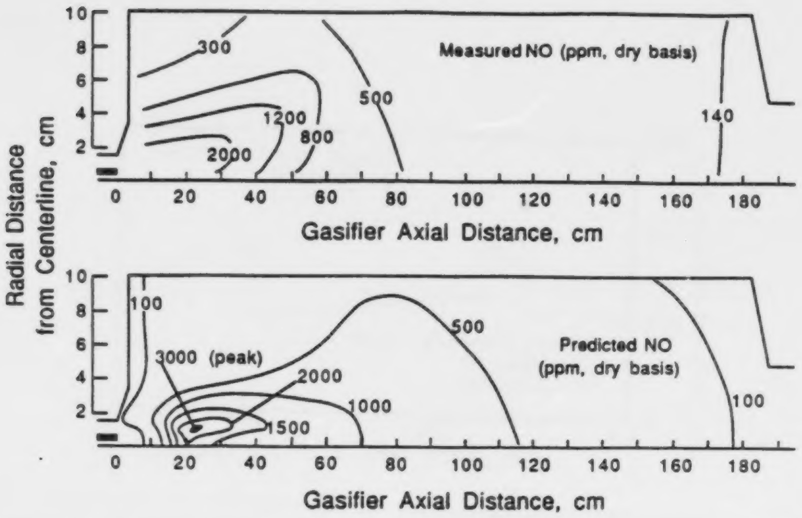


Figure 7. Comparison of predicted and measured NO concentrations during atmospheric gasification of Utah bituminous coal. (Measured data of Brown[39])

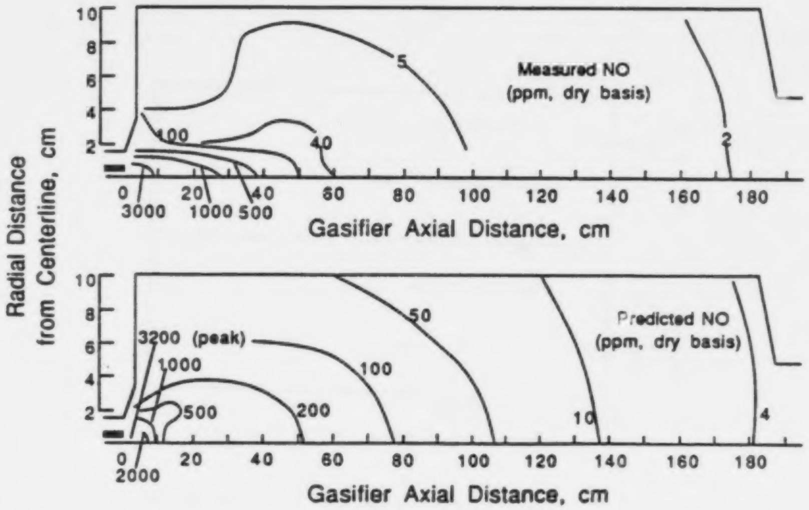


Figure 8. Comparison of predicted and measured NO concentrations during pressurized (5 atm) gasification of Utah bituminous coal. (Measured data of Nichols et al.[40])

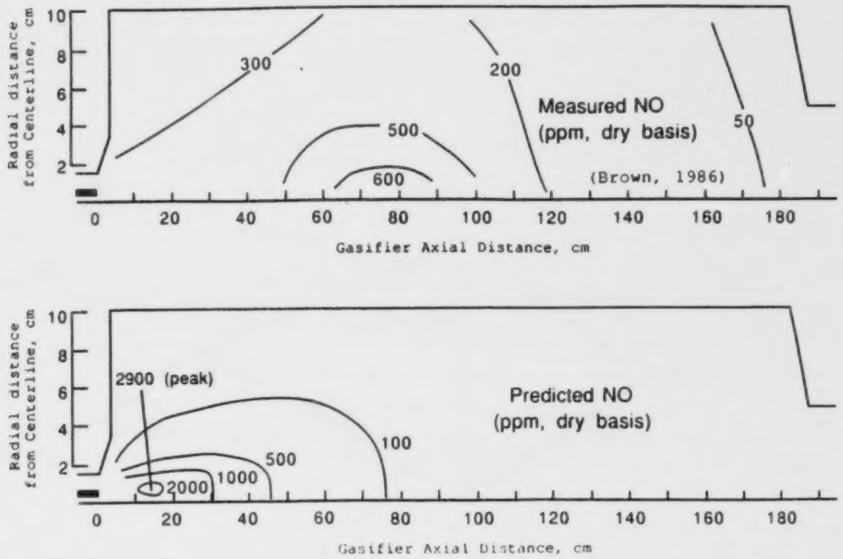


Figure 9. Comparison of predicted and measured NO concentrations during atmospheric gasification of North Dakota lignite. (Measured data of Brown[39])

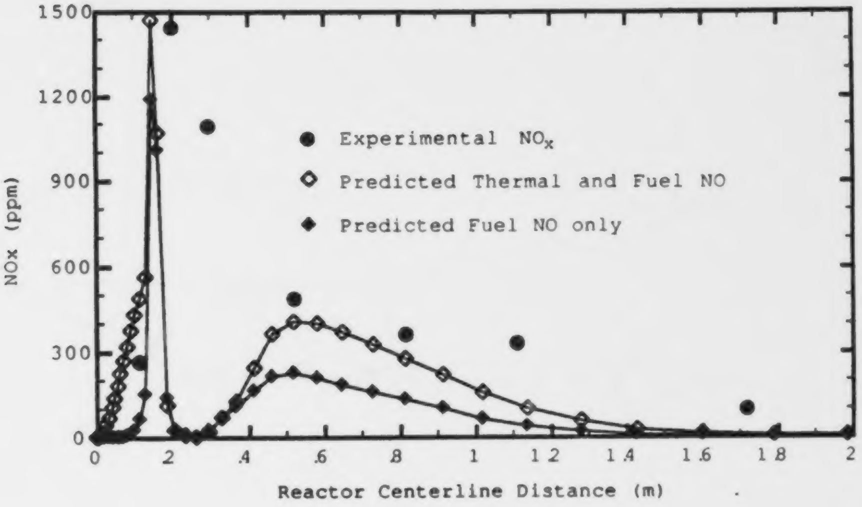


Figure 10. Comparison of predicted fuel NO and joint prediction of thermal and fuel NO with experimental data. (Measured data (circles) of Brown[39])

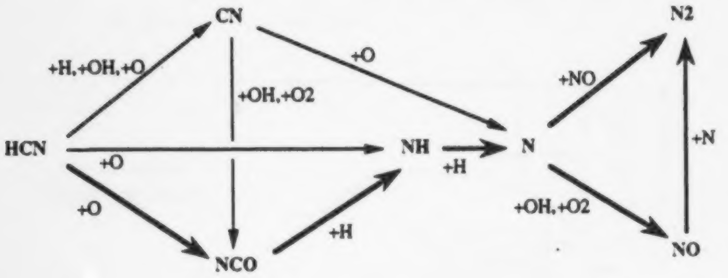


Figure 11. Simplified kinetic mechanism for conversion of fuel nitrogen to NO and N_2. (Source: Miller and Bowman[3])

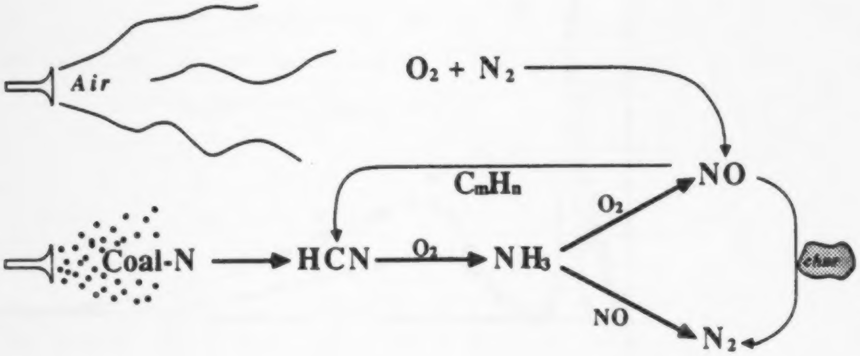


Figure 12. Global fuel NO mechanism correlated by Mitchell and Tarbell[33] to reactor data of Muzio et al.[34]

Reproduced from best available copy.

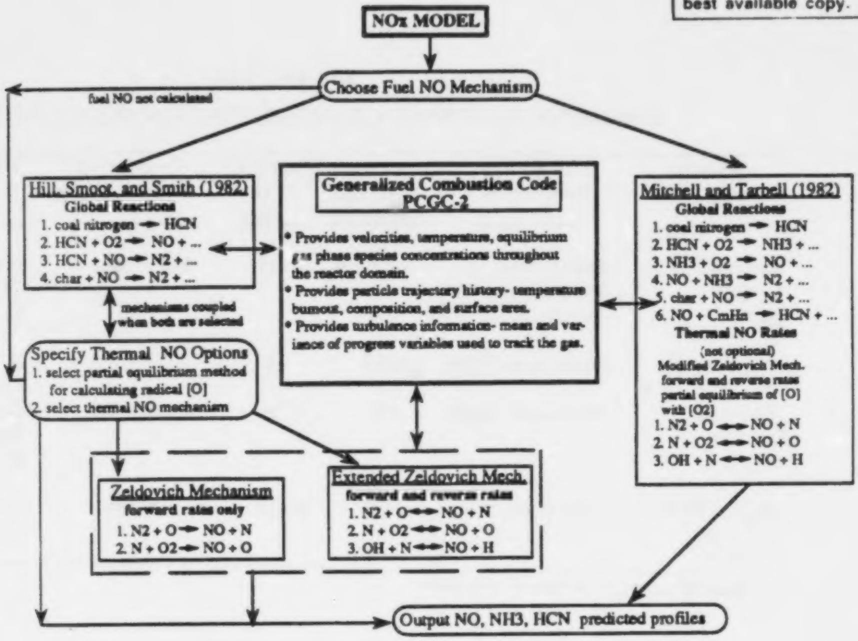

NOx MODEL
Choose Fuel NO Mechanism
fuel NO not calculated
Hill, Smoot, and Smith (1982)
Global Reactions
1. coal nitrogen → HCN
2. HCN + O2 → NO + ...
3. HCN + NO → N2 + ...
4. char + NO → N2 + ...
mechanisms coupled when both are selected
Generalized Combustion Code PCGC-2
• Provides velocities, temperature, equilibrium gas phase species concentrations throughout the reactor domain.
• Provides particle trajectory history- temperature burnout, composition, and surface area.
• Provides turbulence information- mean and variance of progress variables used to track the gas.
Mitchell and Tarbell (1982)
Global Reactions
1. coal nitrogen → HCN
2. HCN + O2 → NH3 + ...
3. NH3 + O2 → NO + ...
4. NO + NH3 → N2 + ...
5. char + NO → N2 + ...
6. NO + CmHn → HCN + ...
Thermal NO Rates
(not optional)
Modified Zeldovich Mech.
forward and reverse rates
partial equilibrium of [O] with [O2]
1. N2 + O ↔ NO + N
2. N + O2 ↔ NO + O
3. OH + N ↔ NO + H
Specify Thermal NO Options
1. select partial equilibrium method for calculating radical [O]
2. select thermal NO mechanism
Zeldovich Mechanism
forward rates only
1. N2 + O → NO + N
2. N + O2 → NO + O
Extended Zeldovich Mech.
forward and reverse rates
1. N2 + O ↔ NO + N
2. N + O2 ↔ NO + O
3. OH + N ↔ NO + H
Output NO, NH3, HCN predicted profiles

Figure 13.Framework of an expanded fuel and thermal NO model coupled with PCGC-2.

Table I. Equation set for NO formation and reduction model in turbulent coal-laden, reacting flow processes.^{1,2}

1.	Mass balance for O_2	(A)	$\tilde{Y}_{O_2} = \tilde{Y}^0_{O_2} - \tilde{Y}_{NO} M_{O_2}/M_{NO}$
2.	Species continuity for i = NO and HCN	(B)	$\bar{\rho}\tilde{u}(\partial \tilde{Y}_i/\partial x) + \bar{\rho}\tilde{v}(\partial \tilde{Y}_i/\partial r) - (\partial/\partial x)(\bar{D}_Y \partial \tilde{Y}_i/\partial x) - (1/r)(\partial/\partial r)(r\bar{D}_Y \partial \tilde{Y}_i/\partial r) = \bar{W}_i$
3.	Overall mean reaction rates for each species	(C)	$\bar{W}_{NO} = (\bar{w}_1 - \bar{w}_2 - \bar{w}_3)M_{NO}$
		(D)	$\bar{W}_{HCN} = (\bar{w}_0 - \bar{w}_1 - \bar{w}_2)M_{HCN}$
4.	Rate of nitrogen release from the coal	(E)	$\bar{w}_0 = \omega_N \bar{S}_p / M_N$
5.	Instantaneous reaction rate terms	(F)	$w_1 = \rho(1 \times 10^{11}) X_{HCN} X^{b}_{O_2} \exp(-67.0\ \mathrm{kcal}/RT)/M_w$
		(G)	$w_2 = \rho(3 \times 10^{12}) X_{HCN} X_{NO} \exp(-60.0\ \mathrm{kcal}/RT)/M_w$
6.	Mean reaction rate term by convolution over probability density functions	(H)	$\bar{w}_i = \bar{\rho} \int_f \int_\eta [w_i(f,\eta)/\rho(f,\eta)]\tilde{P}(f)\tilde{P}(\eta)\, df\, d\eta$
7.	NO–Char reduction reaction	(I)	$\bar{w}_3 = \alpha_p n_p (4.18 \times 10^7) A_E \bar{p}_{NO} \exp(-34.7\ \mathrm{kcal}/R\tilde{T})$
8.	Instantaneous mole fractions	(J)	$X_i = Y_i M_w / M_i$
9.	Instantaneous mass fractions	(K)	$Y_i = \pi_i Y_i'$
10.	Deviation from fully reacted mass fractions	(L)	$\pi_i = \tilde{Y}_i / \tilde{Y}_i'$

Table II.

SUMMARY OF EXPERIMENTAL CASES SELECTED FOR MODEL EVALUATION

Combustion Configuration	Data Source References	Number of Cases/ Figure NO.	Coal Feed Rate (kg/hr)	Reported NO Concentrations	Parameters Investigated
Gasification L=1.89 m D=0.2 m	Brown (1986) Nichols *et al.* (1987) Azuhata *et al.* (1986)	4/7,8,9	35	2-D Profile	Pres. (1-5 atm), Temp., Utah bit., Ill. subbit., N.D. Lig.
Non-Staged	Wendt *et al.* (1978)	3/3,4	5	1-D Profile	S.R. (0.8-1.2), Kentucky bit.,
Air-Staged L=2.2 m D=0.15 m	Wendt *et al.* (1978)	4/5	5	1-D Profile	Secondary-Air Stage Location (0.52s - 0.90 s)
CO_2-O_2 Oxidizer L=2.74 m D=0.6 m	Berry *et al.* (1986)	4/6	30-35	Effluent	CO_2-O_2 ratio Colorado subbit.

L = Reactor Length; D = Reactor Diameter

Table III. Advantages and Limitations of NO_x model Fuel NO Mechanisms.

Hill, Smoot, and Smith Mechanism 1,2

Advantages

1.Global in intermediates, HCN, NO, O_2, all which are measurable

2.Fundamental kinetic parameters obtained by parametric variation of species in a well designed experiment[35]

3.Implicitly accounts for prompt NO formation

Limitations

1.Applicable only to systems where $[HCN] >> ([NO] + [NH_3])$

2.Requires fuel nitrogen to be converter to HCN before decaying to intermediate and product nitrogen species

3.Recycle of NO back to HCN (e.g. reburning) not possible

4.Does not include thermal NO formation

Mitchell and Tarbell Mechanism 33

Advantages

1.Global in intermediates, HCN, NH_3, NO, and O_2

2.Accounts for dependence of reactions on NH_3 concentrations

3.Accounts for recycle of NO to HCN through interaction with C_mH_n.

4.Includes thermal NO in the rate equations

Limitations

1.Kinetic parameters obtained by empirical correlation to relevant species

2.Dependence on C_mH_n sensitive to fuel type with coefficients m and n not explicitly determined

3.Does not acccunt for prompt NO formation either explicitly or implicitly

3.Disallows for thermal and fuel NO effects to be calculated separately

4.Thermal NO rates correlated by assuming partial equilibrium between atomic and molecular oxygen only

NO_x REDUCTION IN FUEL-RICH NATURAL GAS AND METHANOL TURBULENT DIFFUSION FLAMES

M.A. Toqan, J.D. Teare, and J.M. Beér

THE ENERGY LABORATORY
AND
DEPARTMENT OF CHEMICAL ENGINEERING
MASSACHUSETTS INSTITUTE OF TECHNOLOGY

A.J. Weir, Jr. and L.J. Radak
SOUTHERN CALIFORNIA EDISON COMPANY

ABSTRACT

The spatial distribution of NO concentration was determined in 1.0 MW_{th} input fuel-rich methane/air and methanol/air flames in which the combustion air was doped with nitric oxide; the NO concentration in the combustion air was varied between 0.0 to 3200 ppm.

The results show that when the input NO concentration in the combustion air was 1600 ppm the respective NO reduction efficiencies measured in the fuel-rich (ϕ = 1.3) natural gas and methanol flames were 93% and 76%. The reduction efficiency was found to increase with increasing inlet NO concentration; for an inlet NO concentration of 3200 ppm the reduction efficiency in the natural gas flame was 96%.

In a theoretical study, a Sandia chemical kinetic code with kinetic parameters developed by J.M. Levy and B.R. Taylor was used to predict the conversion of nitrogeneous compounds to N_2 in premixed, fuel-rich, plug flow systems as a function of process variables such as initial NO concentration, gas temperature, fuel equivalence ratio, residence time and fuel type. Results of the theoretical computations show that the NO_x reduction process can be considered to consist of two major parts. In the first of these CH_i radicals react with NO to form HCN and subsequently NH_i species, and in the second part hydrogen abstraction of ammonia species by hydrogen results in the formation of molecular nitrogen, N_2. The ultimate reduction level of NO_x is therefore dependent on both the CH_i radical and H atom concentrations. At temperatures > 1700 K the calculated concentrations of these radicals in the CH_4 flame are higher than those predicted for the CH_3OH flame.

The experimental and theoretical results obtained provide information on the effect of fuel type (CH_4 vs CH_3OH) on NO_x reduction with relevance to the "reburn" method, i.e., reduction of NO emission from the combustion of a primary fuel by the injection into its burned gas a hydrocarbon fuel.

INTRODUCTION

The creation of fuel-rich and -lean combustion zones in flames by means of staging the input of either air or fuel is a successful method of NO_x emission control. The degree of conversion of fuel-bound nitrogen (FBN) to molecular nitrogen is determined by the thermodynamics of the system (temperature, pressure and chemical composition of the gas mixture), and the rates of the reactions of nitrogen compounds in the fuel-rich flame zone (1,2,3,4,5). In practical combustion systems the reactions of FBN and NO may be kinetically constrained and provision of sufficient residence time in the fuel-rich zone is therefore essential for high conversion to N_2 (6,7,8). The nitrogenous compounds in the fuel-rich flame zones may have different origins: they may be pyrolysis products of nitrogen-bearing fuels, products of the fixation of atmospheric nitrogen by hydrocarbon fragments early in the flame (9), or the result of reactions due to the secondary injection of hydrocarbons into the NO-containing fuel-lean burned gas. The various pathways for formation and destruction of NO are shown schematically in Figure 1. In the combustion air staging technique, conversion of FBN to N_2 rather than to NO is mainly due to fuel-rich conditions prevailing in the primary flame zone near the burner. In fuel staging, popularly termed "NO-reburn" by Wendt et al., (10) and Myerson(11), hydrocarbon fragments such as CH_2 and CH react with NO to produce HCN and NH_i compounds in a secondary fuel-rich flame zone, with the latter species subsequently being reduced to N_2. A detailed chemical kinetic model which describes this route of NO destruction was extensively tested and validated by Taylor (5) in a flat flame study.

Many experimental and theoretical investigations have been carried out to evaluate the effects of fuel type, equivalence ratio, gas temperature of the reburn stage, and the gas mixture residence time within that zone, on NO_x reburning efficiency. In one series of bench and pilot scale experiments, for example, Chen et al. (12) concluded that NO_x reduction efficiency was best for high NO_x concentration at the end of the primary zone. Residence times of at least 400 ms in the reburn zone were required to favor molecular nitrogen formation. In another study, Lanier and Mulholland (14) investigated the reduction of NO_x by natural gas reburning in a two-dimensional pilot-scale combustion system. An overall reaction order of 1.5 with respect to NO was observed. When the NO concentration in the primary lean stage was low, the "reburn" efficiency was reduced due to the formation of "prompt" NO in the fuel-rich region from the reactions of N_2 with hydrocarbon radicals (as shown in Figure 1). Other researchers (15) also found extensive reductions of nitric oxide in laboratory-scale reactors when combustion products from a fuel-lean primary stage were passed through a fuel-rich secondary stage.

Among the fuels used in "reburn" experiments, natural gas and propane have been found to be better than carbon monoxide, hydrogen and coal. In a demonstration test on a 50 MW utility boiler, Weir et al.(13) found that NO_x emission levels were reduced by more than 50% when methanol was used instead of natural gas as a reburn fuel. These particular results were not readily explainable in terms that could be generalized to other configurations, and thus they provided a motivation for further study.

Motivation of present work

In the present work the primary research objective was to determine the critical parameters which control NO_x reduction efficiencies in turbulent fuel-rich diffusion flames. This was attempted by means of an experimental investigation of NO_x reduction in the flame tunnel of the pilot-scale MIT Combustion Research Facility. The fuel-rich flames were doped with varying amounts of NO which was added to the burner air flow. Because of the utility-boiler results quoted above, natural gas and methanol were chosen as experimental fuels.

In order to further elucidate the factors which control the relative effectiveness of these two fuels in reducing NO to N_2, a parallel theoretical effort was mounted. This effort was confined to plug flow geometries with instantaneous mixing of reactants, but significant insight was obtained from parametric numerical calculations carried out for a number of cases representative of staged combustor conditions.

Direct numerical comparisons of the relative effectiveness of these two fuels are straightforward, since temperature can be chosen to be the same in the cases being compared. Similar comparisons based on experimental data must be viewed with more caution, since several factors which influence the thermal balance within the flow field can introduce some bias into the results. For instance, the lower calorific value of methanol relative to methane implies that greater air preheat would be necessary with the CH_3OH fuel to yield equivalent temperature contours in the flame; a compensative factor is the increased luminosity of the CH_4 flame relative to the blue flame observed with CH_3OH - this induces greater cooling by radiative heat transfer from within the CH_4 flame.

The authors are aware that the doping of the burner air by NO creates conditions in the fuel-rich hydrocarbon flame which are not strictly identical to those in NO reburning. In the latter case the hydrocarbon fuel burns in combustion products which contain CO_2 and H_2O in addition to NO and O_2. There is a larger mass flow of gas with depleted O_2 concentration even though the fuel equivalence ratio is the same as in the fuel-rich hydrocarbon-air flame. It is considered, however, that the effects of these differences upon nitrogen compound interconversion are calculable and that the results of the present study can be applied to NO-reburn systems.

EXPERIMENTAL

The experiments were carried out using the 1.2 m x 1.2 m x 4.5 m test section of the MIT Combustion Research Facility (CRF). The CRF is a pilot scale combustion tunnel equipped with a single, variable-swirl control burner of up to 3 MW_{th} multi-fuel firing capacity, and designed to facilitate detailed investigation of industrial type turbulent diffusion flames. In the experiments, a fraction of the combustion air was introduced through the burner while the rest was injected through eight injectors located 2.44 m downstream of the burner. Figure 2 shows the configuration used in this study.

Experimental Fuels - Operating Conditions

The chemical composition of the natural gas fuel was: CH_4 ~ 97 mole %; CO_2 ~ 0.5%; C_2H_6 ~ 1.6%; C_2H_4 ~ 0.0%; C_3H_8 ~ 0.3%; N_2 ~ 0.3%; and butane and pentane ~ 0.3%. The methanol used was commercial grade, with impurity levels less than 0.5%.

In both flames the thermal input was 1 MW, with fuel flow rates established at 66.8 kg/hr of CH_4, and 163.6 kg/hr of CH_3OH. The burner fuel equivalence ratio and the overall fuel equivalence ratio were maintained at ~ 1.3 and ~ 0.87 respectively; the axial air velocity at burner exit was U_0 ~ 19 m/s for natural gas and 14 m/s for methanol; the swirl number, S, was 0.75, and the combustion air temperature, T_a, was 473 K. Flowfield similarity between the two fuel flames was maintained as closely as possible by choice of fuel nozzle type, using a 70° (full angle) hollow-cone multi-jet gas injector for the CH_4 flame, and a 70° pressure jet hollow-cone single-hole injector for the CH_3OH. The combustion air in the experiments with both fuel types was doped with NO ranging in concentration up to 3200 ppm.

Measurements

In-flame measurements of the spatial distributions of time average values of gas velocity and gas temperature were made using water-cooled impact probes and suction pyrometers respectively. To measure the light hydrocarbons concentrations, gas samples were taken from different locations in the flame by means of water-cooled sampling probes and then analyzed by gas chromatography for stable species concentrations including H_2 and C_1 to C_4 hydrocarbons. NO_x, CO_2, CO and O_2 concentrations in the flame were measured by passing the flame gases through standard chemiluminescent, IR and paramagnetic analyzers.

Experimental Results

The experimental flames were produced by a combination of fuel injection, in the form of a 70° angle hollow-cone spray (methanol) or multi-jet injection of natural gas with the jets subtending the same 70° angle, and a weakly swirling annular air flow surrounding the fuel injectors. The fuel-rich stage created by this configuration was followed by a lean stage in which secondary combustion air was introduced to oxidize the incomplete combustion products such as soot, carbon monoxide and hydrogen (see Figure 2).

To study the effect of inlet NO_x concentration level upon the efficiency of its reduction in the flame the incoming combustion air was doped with various levels of nitric oxide. In the course of the experimental study radial traverses of gas velocities, gas temperatures and chemical species concentrations, including those of major stable species such as NO_x, O_2, CO_2, CO, C_1-C_4 hydrocarbons and H_2, were measured at several axial stations in both the methanol and natural gas flames. The main input variables of the experimental study were:

(1) fuel type - CH_4 or CH_3OH, and
(2) NO_x concentration in the combustion air

Contours of NO_x concentrations without and with doping of the combustion air (1600 ppm NO) and isotherms for the fuel-rich ($\phi = 1.3$) natural gas and methanol flames are shown in Figure 3. The results obtained show that destruction of NO in the natural gas flame is more effective than in the methanol flame. In spite of the attempts to maintain flow field similarity for methanol and natural gas flames, there are significant differences observable. The temperature contours are reasonably similar, but highest NO_x concentrations are found close to the flame axis in the methanol cases, and in an annular off-axis zone for natural gas flames.

In the case when the combustion air was not doped with nitric oxide, it is noteworthy that the minimum NO_x concentration measured at the end of the rich stage was lower for the natural gas (~ 25 ppm) than for the methanol flame (~ 35 ppm).

The variations of CH_4 and H_2 concentrations along the natural gas and methanol flames are shown in Fig. 4. In the methanol flame, the CH_3OH rapidly decomposes primarily to CO and H_2; thus it is significant that CH_4 concentration in the natural gas flame remains substantially higher along most of the flame, by approximately a factor of 10 on the axis, and by more than two orders of magnitude at some off-axis locations. Higher CH_4 concentrations entail also higher CH_i radical concentrations, and these latter are key to the initiation of the NO_x reduction process.

In further experiments the NO concentration in the combustion air was varied to determine the effect of the inlet NO concentration upon the NO destruction efficiency in the fuel-rich flame, with results presented in Fig. 5. Figure 5(A) shows that for an NO concentration level of ~ 3200 ppm in the combustion air a 96% reduction efficiency was attainable in the fuel-rich natural gas flame. As the inlet nitric oxide concentration was reduced the NO reduction efficiency fell; it was 85% for an initial NO concentration of 800 ppm. The measured NO_x concentrations at the exit of the fuel-rich stage are shown as the solid squares in Fig. 5(B); if the secondary air could be admitted without further production of NO_x the dilution would yield lean stage exit concentrations shown as open circles. However, some NO was formed as the secondary air was injected (about 20 ppm), as indicated by the solid circles. This additional NO measured at the exit of the combustor can be attributed to the oxidation of any unconverted NH_i and HCN leaving the rich stage, and/or to thermal NO formation.

THEORETICAL

NO in fuel-rich flames can be destroyed through two main pathways, either by reacting with ammonia (NH_i,N) species to form molecular nitrogen, or by reacting with hydrocarbon radicals such as CH and CH_2 to produce hydrogen cyanide which is further converted to NH_i. The ammonia species thus formed can subsequently reduce NO to N_2.

In order to obtain information on the effect of process variables such as temperature, fuel equivalence ratio and residence time upon the rate of NO reduction, parametric numerical calculations were made assuming plug flow, with instantaneous admixing of fuel into the NO-bearing burned gas.

NO_x Numerical Analysis

A chemical kinetic code developed at Sandia National Laboratory (17) coupled with a differential equation solver developed at Lawrence Livermore Laboratory (18) was used. The code solves the initial value problem for stiff or non-stiff systems of first order differential equations. The equations considered in this study were those for mass conservation of the species. By feeding a temperature profile, a set of species initial mole fractions and a reaction set developed by Taylor(5) (containing 183 reactions including interactions between nitrogenous and hydrocarbon species) into the program, the species mass conservation equations were solved for the different species considered in this study.

Results of Computations

A practical fuel-staged combustion system can comprise several zones, the first of which would typically have fuel-lean stoichiometry. In the so-called "reburn" stage, secondary fuel is injected into the NO-bearing burned gas to change the stoichiometry to fuel-rich. Further downstream in a third stage combustion air is introduced to burn the residual fuel completely; the fuel equivalence ratio is changed to its lean exit value ($\phi < 1.0$).

The present calculations deal with the idealized second-stage of the above process, in which the secondary fuel (CH_4 or CH_3OH) is assumed to be instantaneously mixed with the first-stage combustion products. The latter correspond to the output of a primary fuel-lean flame burning CH_4 with $\phi = 0.90$. The initial gas composition is thus intrinsically fixed, except that both temperature and NO concentration are treated as input parameters for the second-stage calculations, and are varied over wide ranges. Other parameters to be varied in this "reburn" stage are fuel type and fuel equivalence ratio; for each set of parametric choices the subsequent changes in the chemical composition of the reacting mixture are evaluated numerically under conditions of constant temperature.

Comparisons between the CH_4 and CH_3OH cases can be made for any arbitrarily-chosen residence time. In general, the cases using CH_4 as the "reburn" (secondary) fuel approached steady state with a (calculated) residence time on the order of 400-600 ms, but longer times were required to achieve high NO_x reduction levels in the CH_3OH cases. All comparisons discussed below use numerical data obtained for a one-second residence time.

Effect of Temperature

Concentrations of selected species at the outlet of the fuel-rich stage ($\phi = 1.3$) are plotted in Figure 6 for both natural gas and methanol as the "reburn" fuel. The species chosen are NO, NH_3 and HCN, but total fixed nitrogen (TFN) is also plotted, this being the sum of all nitrogenous compounds exclusive of N_2. TFN is important because any species such as NHi or HCN which are present at exit from the "reburn" stage are likely to be oxidized (thus yielding additional NO) during passage through the third stage.

The left-hand side of Figure 6 shows the above species as a function of temperature for CH_4 flames, with three levels of initial NO concentration (800, 100 and 40 ppm) displayed parametrically. The right-hand side of Figure 6 shows similar plots for CH_3OH as the "reburn" fuel, with a single (800 ppm) level of initial NO concentration. For a high initial NO concentration (~800 ppm), and with the reactor temperature maintained at ~ 1900 K, a TFN conversion to N_2 of 97% is obtained for the CH_4 flame (See Figure 7). Both below and above this optimum temperature of 1900 K the TFN yield (and hence the subsequent NO_x emission) increases; at 1400 K the estimated TFN conversion efficiency drops to 8% while above 1900 K the thermal formation of NO_x begins to play a significant role in increasing the total fixed nitrogen leaving the fuel-rich stage in the methane flame.

In the methanol flame the NO_x conversion to N_2 increases continuously as the temperature rises to 2000 K. However, the conversion efficiency reaches only 88% at that temperature.

In Figure 8 the peak values of the sum of CH, CH_2, CH_3 species concentrations in the plug flow reactor, together with the concentration of H atoms at residence times corresponding to the positions of maximum NH_3 concentration, are plotted versus reactor temperature. The differences in NO-to-N_2 conversion between the CH_4 and CH_3OH flames are due to the significantly higher CH_i radical concentrations in the CH_4 flame; these cause an effective NO destruction even at relatively low temperatures (1400 K). It can be concluded from Figure 8 that since the sum of CH_i species concentration is high, the rate-limiting step in the NO-to-N_2 conversion in a CH_4 flame is the reduction of NH_i to N_2 by hydrogen abstraction. In the CH_3OH flame, on the other hand, the lower concentrations of CH_i provide relatively slow rates of conversion of NO to NH_i even at high temperatures (~ 2000 K); however, increase in T is accompanied by increased concentrations of H and OH, and these radicals cause depletion of NH_i species on an increasingly faster time scale, thereby providing the chemical driving force for effective destruction of NO.

Effect of Fuel Equivalence Ratio

Solutions of the model equations for NO_x, NH_3, HCN and TFN concentrations calculated at 1900 K as a function of fuel equivalence ratio are shown in Fig. 9. The two pathways involving CH_i and NH_i species respectively can be seen to affect the course of TFN reduction. The NO-to-N_2 conversion is maximized when the exit value of TFN reaches a minimum; for the CH_4 flame it is seen that with increasing values of ϕ the TFN concentration drops sharply to reach a minimum at $\phi \sim 1.4$ while a similar minimum value occurs at a more fuel-rich stoichiometry ($\phi \sim 1.6$) in the CH_3OH flame. At a low value of ϕ (~ 1.2) the sum of CH_i species concentrations is around 500 ppm in the CH_4 flame and it is less than 1 ppm in the CH_3OH flame. At high values of ϕ (~ 2.0) the CH_4 flame still has higher concentrations of CH_i species, but the presence of high concentration levels of H and OH radicals in the methanol flame again enables effective NO-N_2 conversion, as in the T = 2000 K case discussed above. It is noteworthy that at the optimum fuel equivalence ratios the times required for achieving the plotted reduction levels of NO_x are approximately 550 ms for both fuels.

CONCLUSIONS

- Experiments with NO-doped fuel-rich ($\phi = 1.3$) natural gas and methanol flames showed high levels of NO reduction in both flame types: for the initial NO concentration of ~ 1600 ppm, reduction efficiencies were 93% and 76% in the natural gas and methanol flames, respectively.

- Results of computations of the progress of NO conversion in fuel-rich, premixed, plug flow systems show effects of process variables such as "reburn" fuel type (CH_4 vs CH_3OH), fuel equivalence ratio, temperature and residence time upon NO and TFN conversion to N_2. The computations illustrate the need for high CH_i concentrations in the initial stages of the conversion to form HCN and amine species, followed by high H and OH radicals concentrations to complete the conversion to N_2 by hydrogen abstraction reactions of amines.

- The higher CH_i and H_2 concentrations calculated and measured along the CH_4 flame are congruent with the higher NO reduction efficiencies with this fuel type.

- Calculations indicate that as the fuel equivalence ratio is increased beyond $\phi = 1.6$ (under conditions of constant flame temperatures) the relative advantage of the CH_4 flame diminishes, with NO conversion efficiencies being similar to those obtained in CH_3OH flames.

ACKNOWLEDGEMENTS

Financial support from the Southern California Edison Company and the National Institute of Environmental Health Sciences is gratefully acknowledged. Significant contributions to the experimental research were made by students Tina Bahadori and Tuomas Paloposki and by the CRF technical staff, Don Bash, William Mason and Mark James. Special thanks to Bonnie Caputo for preparing the manuscript.

REFERENCES

(1) Haynes, B.S., The Formation and Behavior of Nitrogen Species in Fuel-rich Hydrocarbon Flames", Ph.D. Thesis, School of Chemical Engineering, University of New South Wales, Australia, December (1975).

(2) Bowman, C.T., Progress in Energy and Combustion Science 1975. Vol. 1 pp. 33-45. Pergamon Press. Oxford, New York.

(3) Sarofim, A.F., Pohl, and Taylor, B.R., "Strategies for Controlling Nitrogen Oxide Emissions During Combustion of Nitrogen Bearing Fuels," AIChE Symposium Series No. 175, 74, 67, (1978).

(4) Levy, J.M. Taylor, B.R. Longwell, J.P. and Sarofim, A.F., "C1 and C2 Chemistry in Rich Mixture, Ethylene-Air Flames", The Nineteenth Symposium on Combustion. The Combustion Institute, Pittsburgh, PA p. 167, 1982.

(5) Taylor, B.R., "Reactions of Nitrogen Species In Fuel-Rich Flames", Sc.D., Department of Chemical Engineering, M.I.T., 1984.

(6) Farmayan, W.F., M.Sc. Thesis, "The Control of Nitrogen Oxides Emission by Staged Combustion," Department of Chemical Engineering, Massachusetts Institute of Technology, Cambridge, MA, April 1980.

(7) Beér, J.M., Jacques, M.T., Farmayan, W.F., and Taylor, B.R., Eighteenth Symposium (International) on Combustion pp. 101-110. The Combustion Institute, Pittsburgh, 1980.

(8) Beér, J.M., M.T. Jacques, Farmayan, W.F., Gupta, A.K., Hanson, S., Rovesti, W.C., "Reduction of NO_x and Solid Emissions by Staged Combustion of Coal Liquid Fuels." Nineteenth Symposium on Coal Liquid, Haifi, Israel, Aug. 1983.

(9) Fenimore, C.P., Thirteenth Symposium (International) on Combustion. The Combustion Institute, 1971, p. 373.

(10) Wendt, J.O.L., Sternling C.V. and Matovich, M.A., Fourteenth Symposium (Internat) on Combustion. Combustion Institute, Pittsburgh, 1971, pp 897-904.

(11) Myerson, A.L.: Fifteenth Symposium (International) on Combustion, p. 1805, The Combustion Institute, 1975.

(12) Chen, S.L., McCarthy, J.M., Clark, W.D., Heap, M.P., Seeker, W.R., and Pershing, D.W., Bench and Pilot Scale Process Evaluation of Reburning for In-Furnace NO_x Reduction, Twenty First Symposium (International) on Combustion, The Combustion Institute, Pittsburgh, 1986.

(13) Weir, A., Jr., L.J. Radak, E.A. Danko R.A. Lewis, and H.W. Buchanan, "Methanol Dual-Fuel Combustion", EPA and EPRI Cosponsored 1987 Joint Symposium on Stationary Combustion NO_x Control, March 23-26, 1987.

(14) Lanier, W.S., and Mulholland, J.A., Application of Reburning for NO_x Control to a Fine tube Package Boiler, Journal of Engineering for Gas Turbines and Power, Vol. 107, 1985.

(15) Clark, W.D., Chen, S.L., Greene, S.B., Seeker, W.R., and Heap, M.P., "Reburning with Pulverized Coal for NO_x Control", Presented at Western States Section of The Combustion Institute Spring Meeting, University of Utah, April 5-6, 1982.

(16) Beér, J.M., W.F. Farmayan, J.D. Teare, M. Toqan, "Laboratory-Scale Study of the Combustion of Coal-derived Liquid Fuels", EPRI Final Report, May 1985.

(17) Kee, R.J., Miller, J.A. and Jefferson, T.H., "CHEMKIN: A General-Purpose Problem-Independent, Transportable, Fortran Chemical Kinetics Code Package", Sandia Laboratories, New Mexico, Doc. No. SAND 80-8003, 1980.

(18) Hindmarsh, A.C., "ODEPACK, A Systematized Collection of ODE Solvers", Numerical Methods for Scientific Computation, August (1982).

(19) Lanier, W.S., Mulholland, J.A., and Beard, J.T., Twenty First Symposium (International) on Combustion, The Combustion Institute, Pittsburgh, 1986.

(20) Miyamae, S., et al., "Evaluation of In-Furnace NO_x Reduction." Proceedings of the 1985 Joint Symposium on Stationary Combustion NO_x Control, May 7, 1985, No. 4-4.

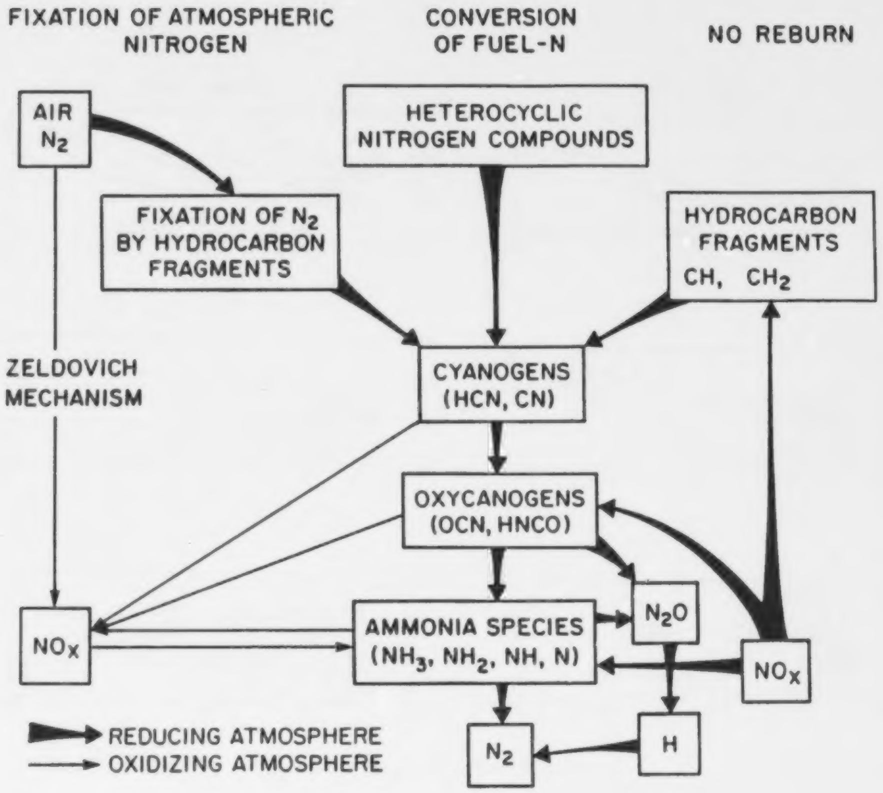

FIXATION OF ATMOSPHERIC NITROGEN
CONVERSION OF FUEL-N
NO REBURN
AIR N_2
HETEROCYCLIC NITROGEN COMPOUNDS
FIXATION OF N_2 BY HYDROCARBON FRAGMENTS
HYDROCARBON FRAGMENTS CH, CH_2
ZELDOVICH MECHANISM
CYANOGENS (HCN, CN)
OXYCANOGENS (OCN, HNCO)
NO_x
AMMONIA SPECIES (NH_3, NH_2, NH, N)
N_2O
NO_x
N_2
H
REDUCING ATMOSPHERE
OXIDIZING ATMOSPHERE

Figure 1. Formation and Reduction of Nitrogen Oxides in Combustion; Mechanistic Pathways

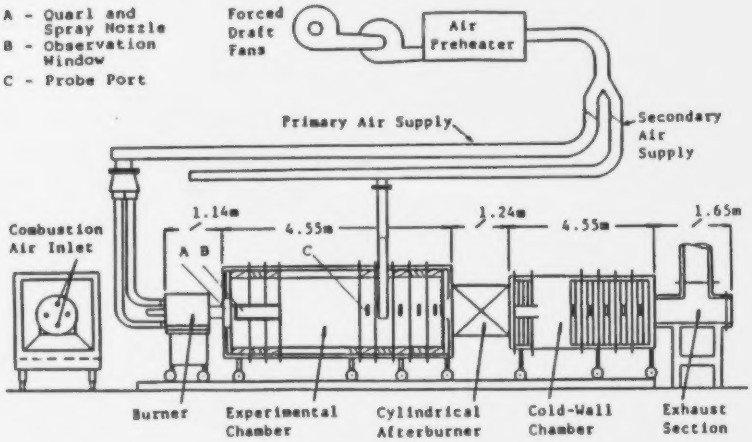


Figure 2. Furnace Assembly and Air Staging System.

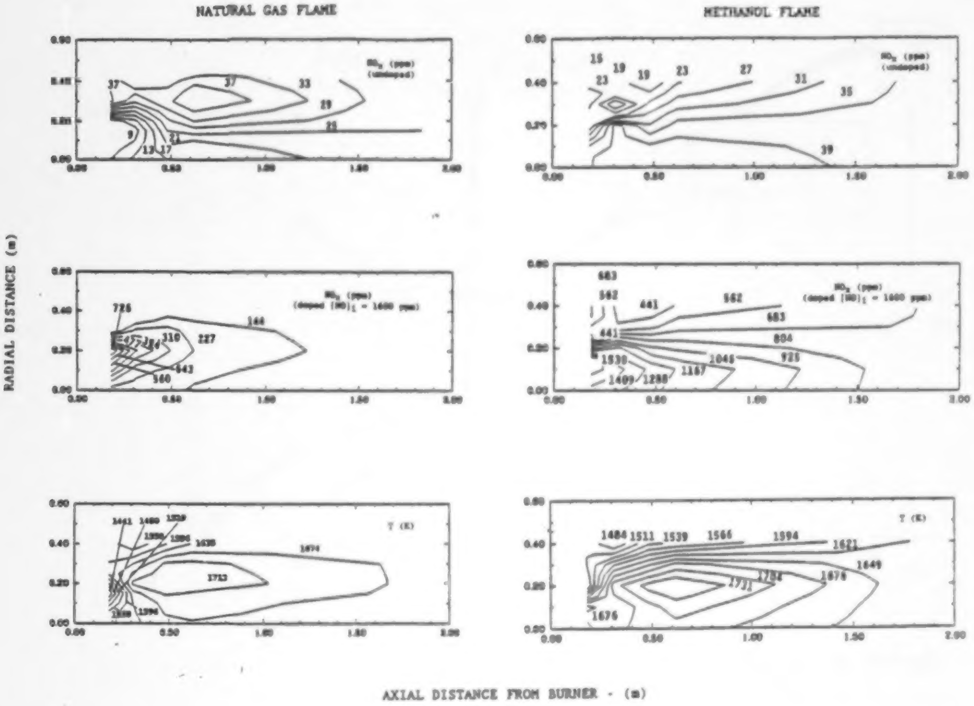


Figure 3. Contours of NO_x concentrations without and with doping of the combustion air (1600 ppm NO) and isotherms for the fuel-rich ($\phi = 1.3$) natural gas and methanol flames.

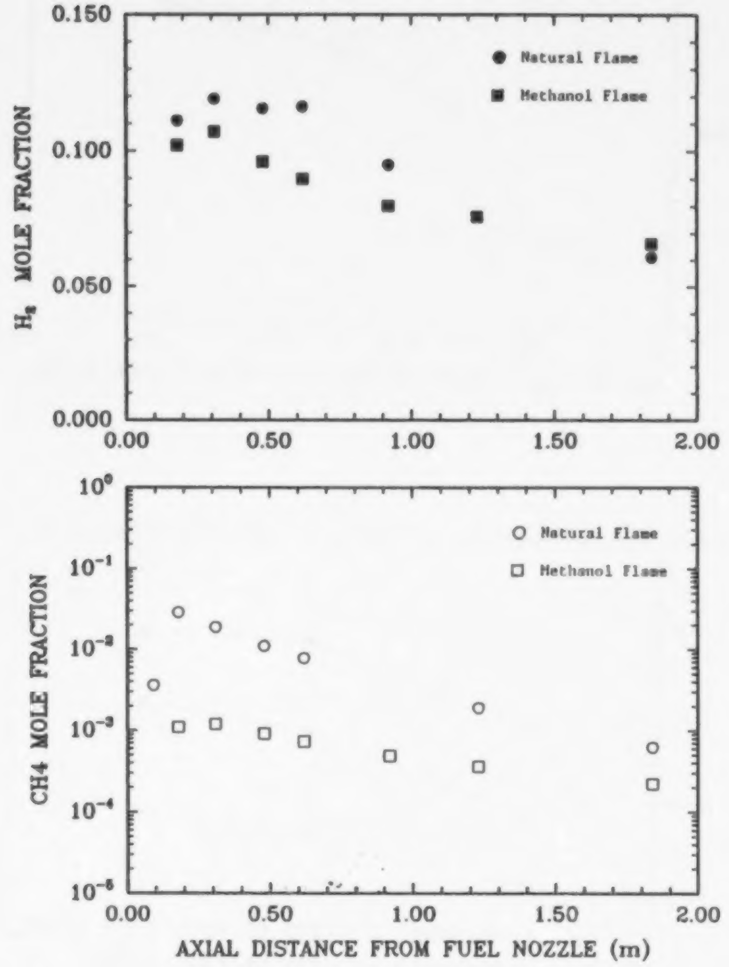


Figure 4. H_2 and CH_4 concentrations along the flame axis in fuel-rich (ϕ = 1.3) natural gas and methanol flames.

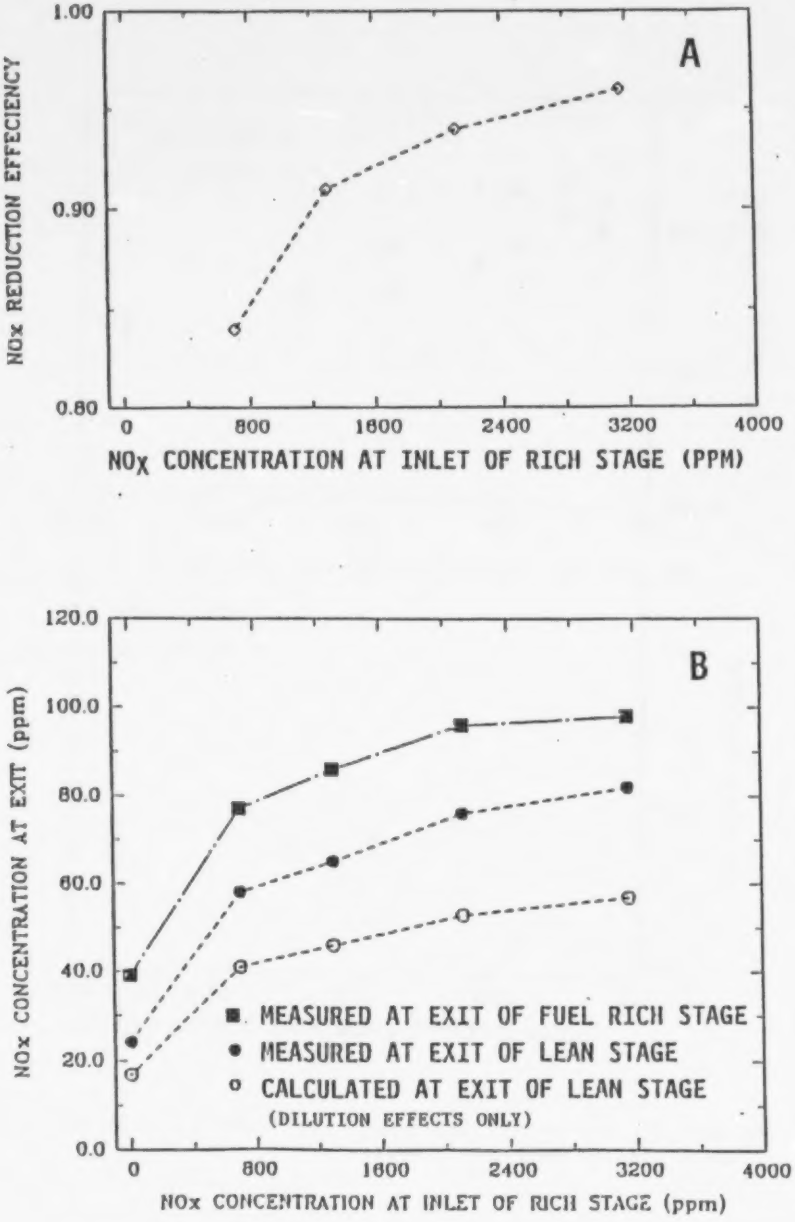


Figure 5. (A) Fractional reduction of NO_x in fuel-rich natural gas flame as a function of the initial NO concentration (introduced with combustion air)

(B) NO_x concentration measured at the end of the natural gas rich stage and at the exit of the combustion tunnel as a function of NO_x concentration entering the fuel-rich stage

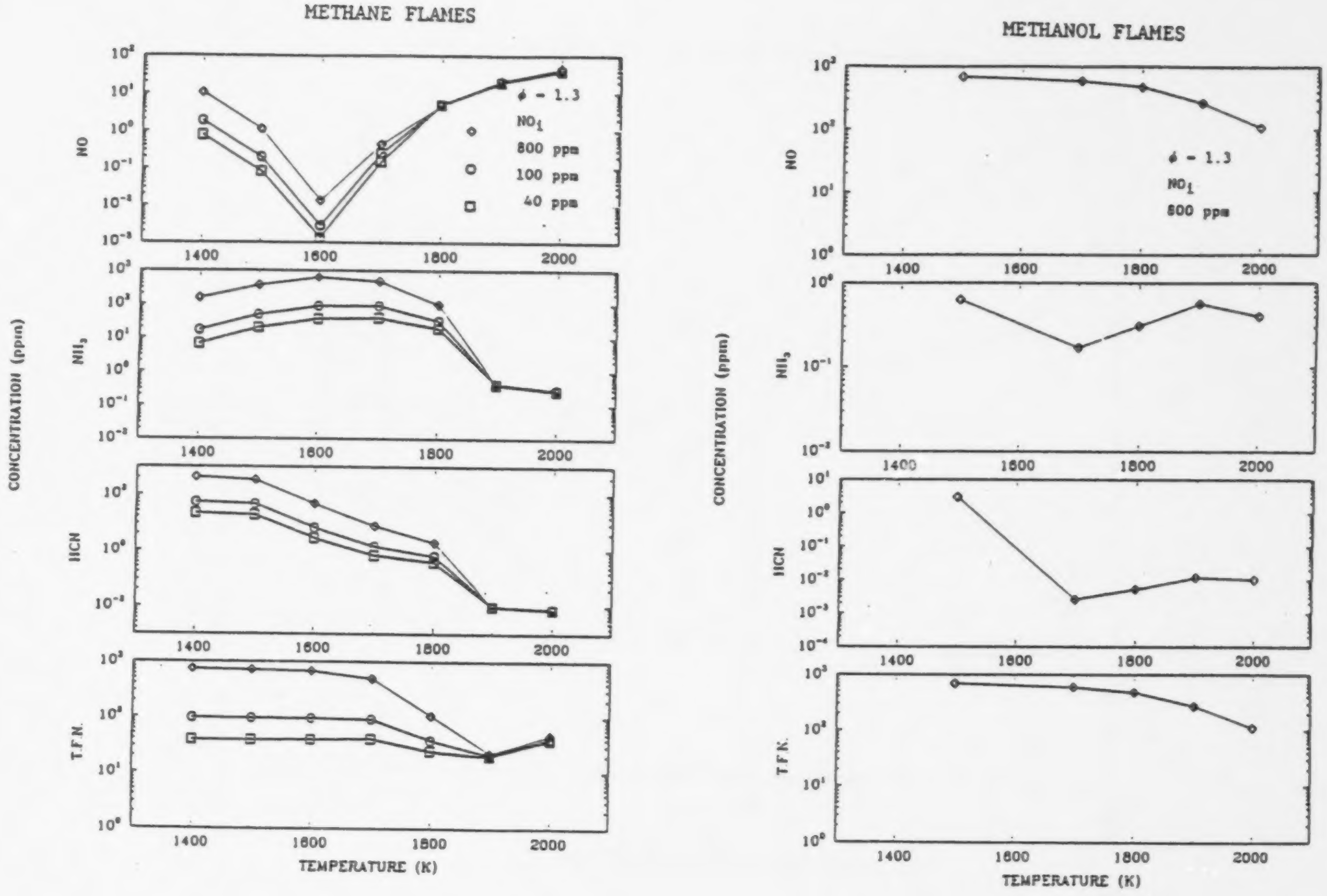


Figure 6. Effect of temperature on NO_x conversion in fuel-rich CH_4 and CH_3OH flames.

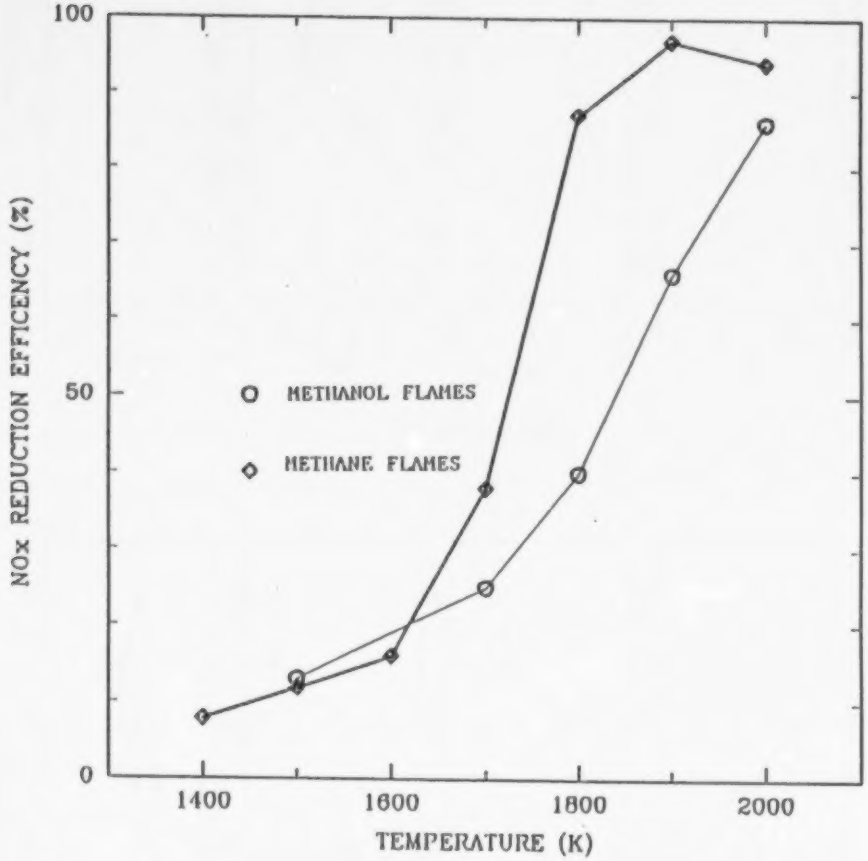


Figure 7. Predicted NO_x reduction efficiency level in both CH_4 and CH_3OH flames as a function of reactor temperature.

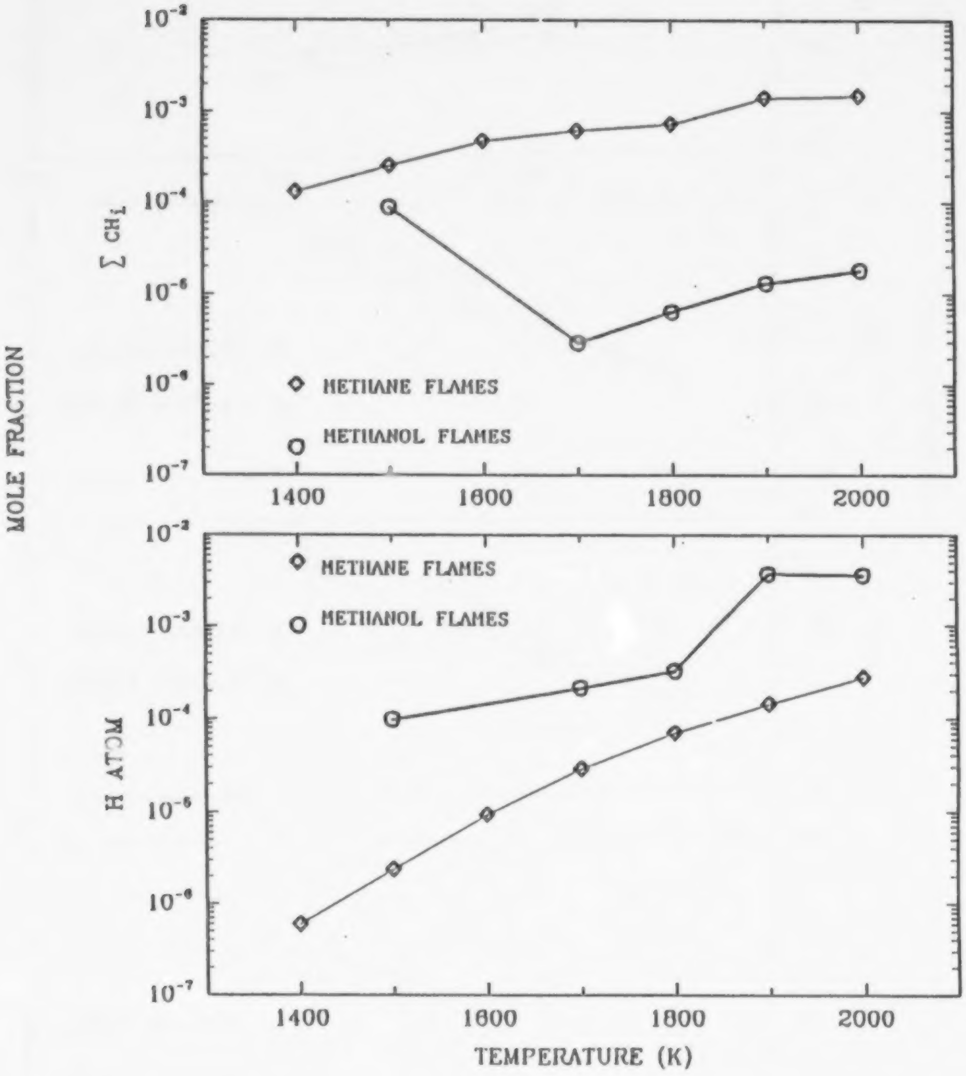


Figure 8. Predictions of peak concentrations of Σ CH_i in the plug flow reactor concentration of H atom at a residence time of peak NH_3 concentration in the reactor.

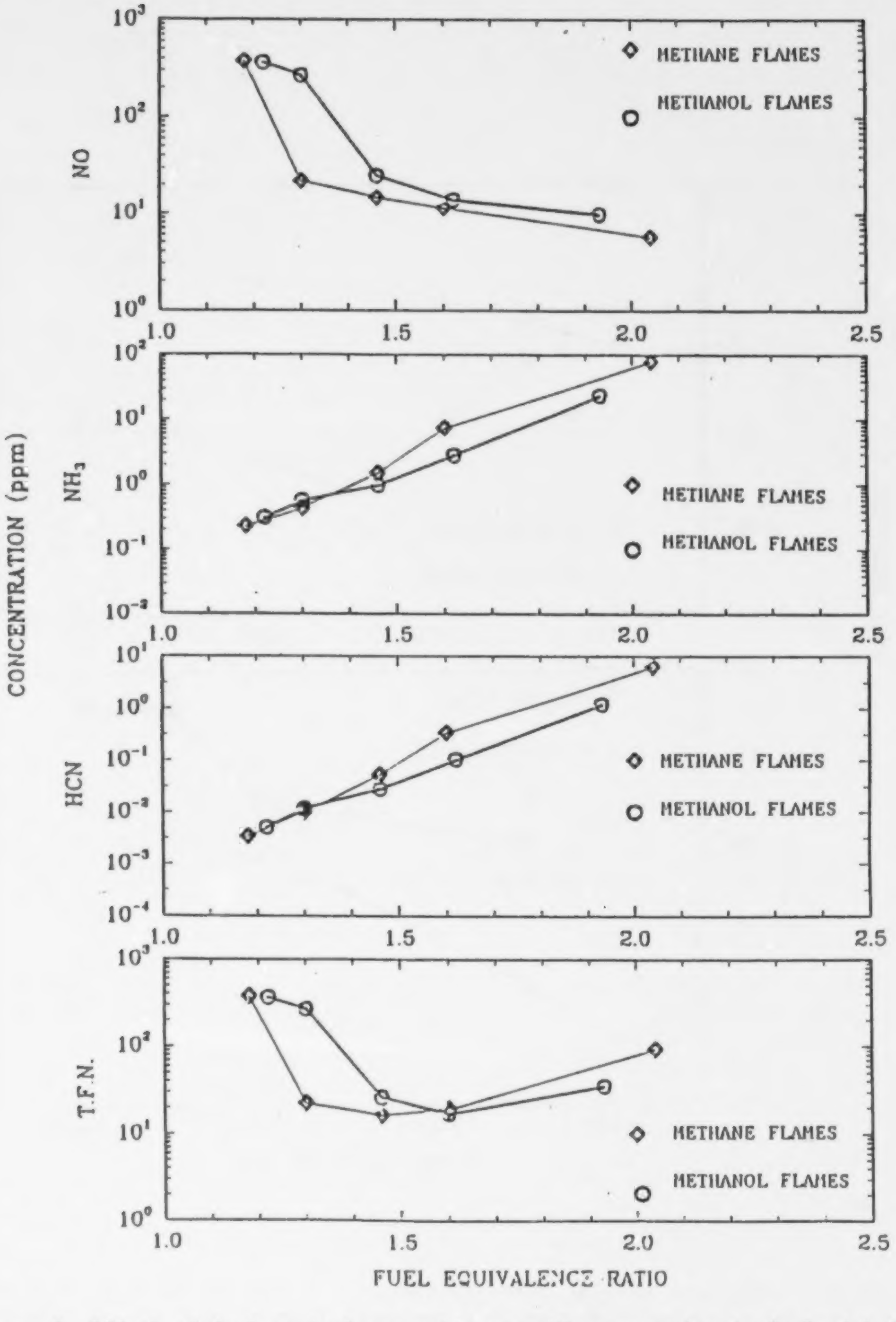


Figure 9. Effect of fuel equivalence ratio upon NO_x conversion in fuel-rich CH_4 and methanol flames.

REDUCTION OF FUEL-NO
BY INCREASED OPERATING PRESSURE
IN A LABORATORY-SCALE COAL GASIFIER

K. M. Nichols
The Institute of Paper Chemistry
Chemical Sciences Division
P.O. Box 1039
Appleton, WI 54912

P. O. Hedman
Brigham Young University
Department of Chemical Engineering
350 CB
Provo, UT 84602

A. U. Blackham
Brigham Young University
Department of Chemistry
Eyring Science Center
Provo, UT 84602

ABSTRACT

Measurements of NO during laboratory-scale gasification of a Utah bituminous coal verified that small increases in pressure (from 1 to 2 atm) at constant residence time resulted in dramatic decreases in effluent NO levels. Tests were conducted at 3 target levels of pressure (1, 2, and 4 atm) and 2 target levels of residence time (450 and 900 ms). Oxygen-to-coal ratio for all tests was 0.90 (SR = 0.45). The dominant factor in causing lower effluent NO levels was the increased kinetic rate of NO decay. Increased residence time in the fuel-rich gasifier contributed to lower effluent NO levels, but was of minor importance when compared to the effect of pressure on the decay rate. Concentrations of N_2 appeared to be slightly increased and concentrations of TFN decreased as pressure was increased. Neither TFN or N_2 concentrations were affected by increasing residence time. For all tests, nitrogen conversion exceeded carbon conversion by about 10%. Neither nitrogen conversion nor carbon conversion was found to increase with increasing pressure. Both increased slightly (4-5%) with increasing residence time, evidence that most of the coal nitrogen and carbon was released during devolatilization.

INTRODUCTION

It has been shown that increased pressure yields lower NO concentrations during combustion. Nichols, et al. [1,2] measured NO levels during gasification of Utah bituminous coal. At 1 atm operating pressure, NO levels were 30 to 300 ppm, depending on oxygen-to-coal ratio, while NO levels at 5 and 10 atm were near zero (less than 10 ppm) regardless of oxygen-to-coal ratio. Heberling and Boyd [3] observed that in overventilated-laminar-diffusion-flames (H_2 and CH_2 fuel doped with CH_3NH_2) the effluent NO levels decreased sharply as pressure was increased. During fluidized bed combustion of a Pittsburgh bituminous coal, Vogel, et al. [4] observed a dramatic decrease in NO concentration (from 1800 to 200 ppm) as combustor pressure was increased (from 1 to 8 atm).

In these studies the observed decreases in NO concentrations were explained by one or more of the following: 1) increased pressure causing a decrease in the level of NO produced in or near the flame front, 2) increased kinetic rate of NO decay due to increased pressure, and 3) increased gas residence time due to increased pressure. Nichols, et al. [1] compared the spatially resolved NO measurements from 5 atm gasification of Utah bituminous coal to the spatially resolved NO measurements from 1 atm gasification of Utah bituminous coal. This comparison was particularly useful for showing that increased gasifier pressure did not result in a decrease in the peak level of NO produced in or near the flame. The observations that effluent NO decreased with increasing gasifier pressure must therefore be explained by 1) the increased rate of NO decay at higher pressure, or 2) the increased residence time at higher pressure, or a combination of these two.

Both of these factors are expected to play an important role, based on the commonly accepted theory of nitrogen chemistry in flames. The overall NO behavior in combustion processes is usually modeled by an overall mechanism for nitrogen speciation similar to that shown here [5-9],

$$\text{fuel-N} \longrightarrow \text{HCN,CN} \longrightarrow \text{NH}_i \begin{array}{l} \xrightarrow{+O_x} \text{NO} \\ \\ \xrightarrow[+\text{NO}]{} N_2 \end{array} \qquad (1)$$

Initially, oxygen is readily available and the NO formation step ($NH_i + O_x \dashrightarrow NO$) dominates over the NO decaying step ($NH_i + NO \dashrightarrow N_2$) yielding a net NO production rate which is rapid and positive. However, the rising NO concentration tends to increase the importance of the NO decay step, while simultaneously the decreasing oxygen concentration tends to decrease the importance of the NO formation step. At some point, the rates of the two steps become equivalent and a peak level of NO is reached. After this, the decay reaction of NO dominates over the formation reaction, yielding a negative net NO production rate (i.e., an NO decay region is reached).

The dominant pathway for the NO decay is generally thought to be of the form

$$-d[NO]/dt = k[NO][NH_i] \qquad (2)$$

though the nature of the intermediate, NH_i, is the subject of various opinions. Dividing both sides of Equation 2 by [NO], and writing $[NH_i]$ as the mole fraction of NH_i times the total concentration (using the ideal gas law) gives

$$-d(\ln[NO])/dt = kY_{NH_i}P/(RT) \qquad (3)$$

Equation 3 suggests that for negligible changes in k, Y_{NH_i}, and T, the decay rate of the logarithm of NO concentration should increase approximately in proportion to increasing pressure. Thus, small increases in pressure should cause large increases in the rate of NO decay.

Increased residence time should also decrease effluent NO levels at a given decay rate, by providing a greater length of time for the hot gases to remain in the region of net NO decay. Experimental data are lacking to show which of these two effects is more pronounced. Variations in these two variables (pressure and residence time) were confounded in the previous experiments. That is, pressure was not altered independently of residence time.

OBJECTIVE

The objective of this study was to further quantify the relative importance between the effect of residence time on NO levels, and the effect of pressure on NO levels. To accomplish this, a set of experiments were designed and executed with the BYU gasifier using Utah bituminous coal. The goal of these experiments was to obtain NO measurements under conditions where 1) pressure was varied while residence time was maintained constant, and 2) residence time was varied while pressure was maintained constant.

EXPERIMENTAL

Gasifier

The experiments were conducted in the BYU laboratory-scale entrained-coal gasifier. The gasifier (see Figure 1) has been described in detail previously [10-12]. It was axisymmetric, fired downward and consisted of six flanged-sections of 12 in. (30.5 cm) nominal diameter steel pipe, 30.5 cm each in length, and one flanged section 15.2 cm in length. Each of the six, full length sections was equipped with an access port which could be used either for insertion of a sample collection probe or for attachment of a quartz sight-window. Castable ceramic (5.1 cm thickness) lined the interior of each section, and the reactor top and bottom, and the access ports. Inside reactor diameter and length were 20 cm and 189 cm respectively.

High purity oxygen (99.6 mol%, the balance being argon) was fed from a bank of high pressure cylinders. The use of pure oxygen provided an environment where the only source of nitrogen was the coal-nitrogen. The pulverized coal was withdrawn from the pressurized feeder by an auger and entrained in an argon stream which conveyed the coal into the injector. The coal feed rate was accurately monitored by suspending the feed system on a balance beam using a counter weight [13]. A load cell attached to the beam indicated the weight (or weight change) in the hopper.

Sample Collection

A water quenched, stainless steel probe (see Figure 2) was used to collect gas-liquid-solid samples from the gasifier. It has been shown [14] by comparing the results from sampling with quartz probes to the results from sampling with stainless steel probes, that stainless steel does not significantly affect nitrogen species sampled from combustion.

The sample separation system (see Figure 3) divided the sample for chemical analyses. The quenched sample first passed through a gas-liquid disengager. The gas was then passed through an ice bath and any further condensate was removed by a second gas-liquid disengager. The remaining gas was passed through a 2 mm filter which removed remaining particulate matter. The liquid was collected, and also filtered with a 0.8 mm filter to remove particulate matter.

Analytical Methods

The analytical procedures developed previously [15-17] were used to determine nitrogen species concentrations (N_2, NO, NH_3, and HCN) as well as major gas species in the gas and liquid phases, and the elemental composition in the solid phase. The liquid phase was analyzed for NH_3 and HCN as NH_3 and CN^- ion using specific gas and ion electrodes. The N_2 in the gas phase was determined using a gas chromatograph equipped with a thermal conductivity detector while the NO was determined using a chemiluminescence NO analyzer.

Elemental analyzers, which combust the solid sample were used to determine the carbon, hydrogen, nitrogen, sulfur, and ash content of the raw coal and char samples. The chemical analyses were performed as soon after each test as possible to minimize any error caused by continued reaction or decay of species. Steps were taken to chemically preserve each species.

Test Plan

To determine the relative importance of pressure and residence time on effluent NO levels, a test design was planned and performed which included 3 target levels of pressure (1, 2, and 4 atm) and 2 target levels of residence time (450 and 900 ms). The other parameters were maintained constant. The target oxygen-to-coal mass ratio for all tests was 0.9 (equivalent to a stoichiometric ratio of near 0.4).

Concentrations of NO were measured at each of the combinations of pressure and residence time. Replicate measurements were made to obtain a measure of the reproducibility of the data. The residence time was controlled by adjusting the combined oxygen-plus-coal feed rate. At a given pressure, for instance, the residence time was doubled by halving the combined feed rate.

Test Coal

The coal for these gasification experiments was a high volatile Utah bituminous coal obtained from the Valley Camp Mine. It was pulverized to a mean particle size of near 50 µm. Size data, elemental composition and other physical characteristics are shown in Table 1.

RESULTS AND DISCUSSION

NO Measurements

Figure 4 shows the effluent NO measurements from these tests. Because the actual pressure and residence time values achieved varied somewhat from the target levels, these NO measurements are plotted as a function of both variables; residence time in Figure 4a, and pressure in Figure 4b. In Figure 4a, the actual (measured) value for the pressure (in atm) is noted next to each data symbol. In Figure 4b, the actual (estimated) value for the residence time (in ms) is noted next to each symbol.

The residence time values were estimated from the following equation

$$t = [AP/(RG)](1/a)\ln[(ax + b)/b] \qquad (4)$$

where A was gasifier cross sectional area, P was gasifier pressure, R was the ideal gas constant, G was the molar flow rate of gas, x was axial distance from injector tip, and a and b were parameters in the temperature function $T = ax + b$. The particular values used for a and b were -7.5 K/cm and 2800 K. The derivation of Equation 4 is given by Nichols, et al. [1]. The assumption of a linear function for temperature was evaluated by comparing the resulting residence time values to the residence time values calculated by using more complex temperature functions. Residence time values were not significantly different, so the more simple linear temperature function was chosen. The assumption of constant gas flow rate appears justified based on earlier observations that most of the coal mass is released to the gas phase early in the flame, during devolatilization [18,19].

Levels of NO were dramatically influenced by pressure, but the influence of residence time was secondary. Increasing pressure from 1 atm to approximately 2 atm caused effluent NO levels to decrease from an average of 230 to 12 ppm. Increasing the pressure to 4 atm further reduced NO to about 2 ppm.

Two of the one atm data points near 400 ms in Figure 4a show a lower NO concentration than the 1 atm data points at greater residence times. At first it appears that NO concentration increased with increasing residence time, which seems unlikely. This is, however, explained by the slightly greater than 1 atm pressure (1.06 and 1.08 atm) corresponding to these data points. This strong dependence of NO concentration on pressure is illustrated particularly well in Figure 4b. Effluent NO concenration was extremely sensitive to pressure between 1 and 2 atm. This illustrates a potential NO_x reduction method for any combined cycle or staged combustion process, wherein the first fuel rich stage could be slightly pressurized. It also illustrates a potential method for enhancing any NO_x reduction method which relies on the reaction of NO with another nitrogen containing species to form N_2.

A strong dependence of NO concentration on residence time was not seen over the range of residence times of these experiments. The 1 atm NO concentration values near the target residence time of 450 ms were 225 and 240 ppm (see Figure 4a), while the 1 atm NO values near 900 ms residence time were 210 ppm. This slight decrease in NO concentration was probably due to the slight increase in pressure, and not to the increased residence time. Even if the slight decrease in NO concentration was attributed completely to increased residence time, the effect of residence time would still be secondary or even negligible compared to the effect of increased pressure on effluent NO concentration.

TFN and N_2 Measurements

The TFN ($HCN + NH_3 + NO$) and N_2 concentrations for these same tests are reported in Figures 5 and 6 respectively. The concentrations of TFN appear to have decreased with increasing pressure, while concentrations of N_2 appear to have increased. Residence time had no consistent effect on TFN or N_2 levels.

Since the decay of NO is by reaction of NO with other nitrogen species, it is expected that increasing pressure would have resulted in decreased TFN concentrations and increased N_2 concentrations. It is expected that if the measurement errors were decreased, these trends would have been more clearly evident.

Nitrogen Conversion

The measured nitrogen and carbon conversion values are shown in Figure 7. Nitrogen (or carbon) conversion is defined to be the percent of fuel nitrogen (or carbon) which was converted from the coal to gas phase species. These values were determined by measuring the nitrogen, carbon and ash in the raw coal, as well as in the collected char samples, and using ash as an inert tracer. Azuhata, et al. [20] used argon tracer gas, as well as ash measurements for determination of carbon conversion during entrained flow gasification of Utah bituminous coal. The carbon conversion values based on argon agreed well with those based on ash, showing the validity of using ash as an inert tracer for determination of elemental conversions during gasification.

For all tests, nitrogen conversion exceeded carbon conversion by 8-10%. This is consistent with previous gasification measurements [1,16]. Malte and Rees

[21] reported the ratio of nitrogen conversion to carbon conversion to be between 1.3 and 2.0 for coal gasification. Of course this ratio must approach unity as carbon conversion approaches 100%.

An explanation for nitrogen conversion exceeding carbon conversion is the behavior of coal nitrogen evolution with temperature. Carefully controlled coal pyrolysis experiments [18,22] have shown that nitrogen evolution is more sensitive to temperature than total mass evolution. For the gasifier of this study, residence times varied from 400 to 1000 ms. Peak local temperatures in the gasifier were probably near the maximum adiabatic flame temperature (at SR = 1.0), which was calculated to be about 3200 K (at 1 atm). It appears that sufficiently high temperatures existed for a sufficient length of time to cause the more temperature sensitive nitrogen conversion to exceed the less temperature sensitive carbon conversion.

Neither nitrogen conversion nor carbon conversion was found to depend on pressure. Both increased only slightly with increasing residence time. This provides evidence that most of the coal nitrogen and carbon are released during devolatilization. If significant nitrogen were released during char oxidation, the increased residence time would have had a greater impact on nitrogen conversion.

Temperature

The possibility that gasifier temperature was not constant among these tests needs to be addressed. For adiabatic conditions, equilibruim calculations show that flame temperatures are somewhat higher for higher values of pressure. For pressures of 1 and 4 atm, adiabatic temperatures are 2560 K and 2600 K respectively at the oxygen-to-coal ratio of 0.90 (SR = 0.45) used for these gasifier tests, and maximum adiabatic temperatures (at SR = 1.0) are 3070 K and 3250 K respectively.

The gasifier used for these experiments was, however, not adiabatic. The heat loss for these tests was estimated to be approximately 20-25% of the heat released from the coal. This was due to the relatively large ratio of surface area to volume resulting from the relatively small scale of the equipment.

The dramatic decreases in NO concentrations occurred as pressure increased from 1 to 2 atm. For this pressure increase, adiabatic calculations yielded an 11 K temperature rise at SR = 0.45, and a 41 K temperature rise at SR = 1.0. These temperature rises are relatively small even for adiabatic conditions, and would be smaller yet for non-adiabatic conditions. The gasifier temperatures were more likely controlled by factors other than pressure; factors such as oxygen-to-coal ratio and heat loss. The observation in Figure 7 that carbon conversion was not affected by pressure also suggests that temperature changes were negligible since carbon conversion is known to be temperature dependent.

Temperature measurements were recorded from the gasifier exit, near the gas sampling location, using a thermocouple. These uncorrected thermocouple readings averaged approximately 1500 K, and showed no significant increase in temperature with increasing pressure. These thermocouple measurements were, however, not deemed very reliable due to the difficulty of determining the convective and radiative effects on the thermocouple reading.

Major Gas Species

It is also important to consider what happened to the levels of the major gas species (CO, H_2, and CH_4) as pressure and residence time were varied. This effect is seen by calculating the energy content of the product gas, which results from the heats of combustion of the primary combustible constituents, CO, H_2, and CH_4. Figure 8 shows that the differences in energy content among the 3 pressure levels were negligible. This suggests that increasing pressure from 1 to 4 atm had little effect on the gasifier performance. At all 3 pressures, the energy content of the product gas decreased approximately 5 kJ per kg for each ms increase in residence time.

CONCLUSIONS

1) During gasification, small increases in pressure (i.e., from 1 atm to 2 atm operating pressure) resulted in dramatic decreases in effluent NO levels, at all levels of residence time and coal feed rate tested.

2) The dominant factor in causing lower effluent NO levels with increased pressure was the increased kinetic rate of NO decay. Increased residence time in the fuel rich gasifier contributed to lower effluent NO, but was of minor importance when compared to the effect of pressure. The peak NO level reached in or near the gasifier flame was not decreased by increasing pressure. On the contrary, it was slightly increased, as shown by previous studies.

3) Concentrations of TFN (HCN + NH_3 + NO) showed some decrease with increasing pressure, while concentrations of N_2 showed some increase with increasing pressure.

4) In all cases, nitrogen conversion exceeded carbon conversion, typically by about 10 percent.

5) Neither nitrogen conversion nor carbon conversion was found to increase with increasing pressure. Both increased only slightly (4-5%) with increasing residence time. This was evidence that the bulk of the coal nitrogen and carbon was released during devolatilization.

6) Experimental temperature measurements did not show gasifier temperature to vary with pressure or residence time. Equilibrium calculations show that for a non-adiabatic reactor, increasing pressure from 1 to 2 atm will yield insignificant temperature rises.

7) The energy content contained in the combustible species of the product gas was not affected by pressure, but decreased with increasing residence time, at about 5 kJ/kg·ms.

ACKNOWLEDGEMENTS

This work was supported primarily by the U. S. Department of Energy, Morgantown Energy Technology Center, Morgantown, West Virginia with Gary Friggens and Leland Paulson as technical project officers. Financial Support of the Research Division and the College of Engineering and Technology of Brigham Young University is also acknowledged.

REFERENCES

1. Nichols, K. M., Hedman, P. O., and Smoot, L. D., "Release and Reactions of Fuel-Nitrogen in a High-Pressure Entrained-Coal Gasifier," *Fuel*, Vol 66, (1987): see also Nichols, K. M. 'The Effects of Elevated Pressure on the Formation of Nitrogen and Sulfur Pollutants During Entrained Coal Gasification,' M. S. Thesis, Department of Chemical Engineering, Brigham Young University, Provo, Utah 84602 (1985)

2. Nichols, K.M., 'Nitrogen Pollutant Formation in a High-Pressure Entrained-Coal Gasifier,' Ph. D. Dissertation, Department of Chemical Engineering, Brigham Young University, Provo, Utah 84602 (1987)

3. Heberling, Paul V., and Boyd, Michael G., 'The Effects of Pressure on NO yield from Fuel-N in Laminar Diffusion Flames,' *Comb. and Flame*, Vol 41, p 331 (1981)

4. Vogel, G.J., Swift, W.M., Lenc, J.F., Cunningham, P.T., Wilson, W.I., Pank, A.F., Teats, F.G., and Jonke, A.A., 'Reduction of Atmospheric Pollution by the Application of Fluidized-Bed Combustion and Regeneration of Sulfur Containing Additives,' Report EPA-650/2-74-104 (1974)

5. Haynes, B.S., 'Reactions of Ammonia and Nitric Oxide in the Burnt Gases of Fuel-Rich Hydrocarbon-Air Flames,' *Comb. and Flame*, Vol 28, p 81 (1977)

6. De Soete, G.G., 'Overall Reaction Rates of NO and N_2 Formation from Fuel Nitrogen,' *Fifteenth Symposium (International) on Combustion*, The Combustion Institute, Pittsburgh, PA, p 1093 (1975)

7. Fenimore, C.P., 'Studies of Fuel-Nitrogen Species in Rich Flame Gases,' *Seventeenth Symposium (International) on Combustion*, The Combustion Institute, Pittsburgh, PA, p 661 (1979)

8. Miller, J.A., Branch, B.C., McLean, W.J., Chandler, D.W., Smooke, M.D., and Kee, R.J., 'The Conversion of HCN to NO and N_2 in H_2-O_2-HCN-AR Flames at Low Pressure,' *Twentieth Symposium (International) on Combustion*, The Combustion Institute, Pittsburgh, PA, p 673 (1984)

9. Glass, J.W., and Wendt, J.O.L., 'Mechanisms Governing the Destruction of Nitrogeneous Species During the Fuel Rich Combustion of Pulverized Coal,' *Nineteenth Symposium (International) on Combustion*, The Combustion Institute, Pittsburgh, PA, p 1243 (1982)

10. Skinner, F.D., '1980 ASME Winter Annual Meeting,' New York, 1980: see also Skinner, F.D., Ph.D. Dissertation, Department of Chemical Engineering, Brigham Young University, Provo, Utah 84602 (1980)

11. Soelberg, N.R., Smoot, L.D., and Hedman, P.O., 'Entrained Flow Gasification of Coal: 1. Evaluation of Mixing and Reaction Processes from Local Measurements,' *Fuel*, vol 64, p 776 (1985): see also Soelberg, N.R., 'Local Measurements in an Entrained Flow Gasifier,' M.S. Thesis, Department of Chemical Engineering, Provo, Utah (1983)

12. Brown, B.B., Smoot, L.D., and Hedman, P.O., 'Effect of Coal Type on Entrained Gasification,' *Fuel*, vol 65, p 673 (1986): see also Brown, B.B., 'Effect of Coal Type on Entrained Gasification,' Ph.D. Dissertation, Department of Chemical Engineering, Brigham Young University, Provo, Utah (985)

13. Cope, R.F., 'The Effects of Coal Rank in a Pressurized Entrained Coal Gasifier,' M.S. Thesis, Department of Chemical Engineering, Brigham Young University, Provo, Utah (1987)

14. Zabielski, M.F., Dodge, L.G., Colket, M.B., and Seery, D.J., 'The Optical and Probe Measurement of NO: A Comparative Study,' *Eighteenth Symposium (International) on Combustion*, The Combustion Institute, Pittsburgh, PA, p 1591 (1981)

15. Price T.D., Smoot, L.D., and Hedman, P.O., 'Measurement of Nitrogen and Sulfur Pollutants in an Entrained-Coal Gasifier,' *Ind. Eng. Chem. Fundam.*, vol 22, p 110 (1983): see also Price, T.D., 'Measurements of Pollutants in an Entrained-Flow Coal Gasifier,' M.S. Thesis, Department of Chemical Engineering, Brigham Young University, Provo, Utah (1981)

16. Highsmith, J.R., Soelberg, N.R., Hedman, P.O., Smoot, L.D., and Blackham, A.U., 'Entrained Flow Gasification of Coal: 2. Fate of Nitrogen and Sulfphur Pollutants as Assessed from Local Measurements,' *Fuel*, vol 64, p 782 (1985): see also Highsmith, J.R., 'Fate of Fuel Nitrogen and Sulfur During Coal Gasification: Detailed Local Pollutant Measurements in an Entrained Coal Gasifier,' M.S. Thesis, Department of Chemical Engineering, Brigham Young University, Provo, Utah (1982)

17. Burkinshaw, J.R., Smoot, L.D., and Hedman, P.O. and Blackham A.U., 'Analysis of Sulfur Pollutants in Three-Phase Coal Combustion Effluent Samples,' *Ind. Eng. Chem. Fund.*, vol 22, p 292 (1983): see also Burkinshaw, J.R., 'The Analysis of Sulfur Pollutants From An Entrained-Flow Coal Combustor,' M.S. Thesis, Department of Chemical Engineering, Brigham Young University, Provo, Utah (1981)

18. Pohl, J.H., and Sarofim, A.F., 'Devolatilization and Oxidation of Coal Nitrogen,' *Sixteenth Symposium (International) on Combustion*, The Combustion Institute, Pittsburgh, PA, p 491 (1977)

19. Peck, R.E., Midkiff, K.C., and Altenkirch, R.A., 'The Evolution of Nitrogen From Pulverized Subbituminous Coal Burnt in a One-Dimensional Flame,' *Twentieth Symposium (International) on Combustion*, The Combustion Institute, Pittsburgh, PA, p 1373 (1984)

20. Azuhata, S., Hedman, P.O. and Smoot, L.D. 'Carbon Conversion in an Atmospheric-Pressure Entrained Coal Gasifier,' *Fuel*, vol 65, p 221 (1986)

21. Malte, P.D., and Rees, D.P., 'Mechanisms and Kinetics of Pollutant Formation During Reaction of Pulverized Coal,' chapter 11 of Pulverized Coal Combustion and Gasification, Smoot, L.D., and Pratt, P.T., eds., Plenum Publishing Company, NY (1979)

22. Blair, D.W., Wendt, J.O.L., and Bartok, W., 'Evolution of Nitrogen and Other Species During Controlled Pyrolysis of Coal,' *Sixteenth Symposium (International) on Combustion*, The Combustion Institute, Pittsburgh, PA, p 475 (1977)

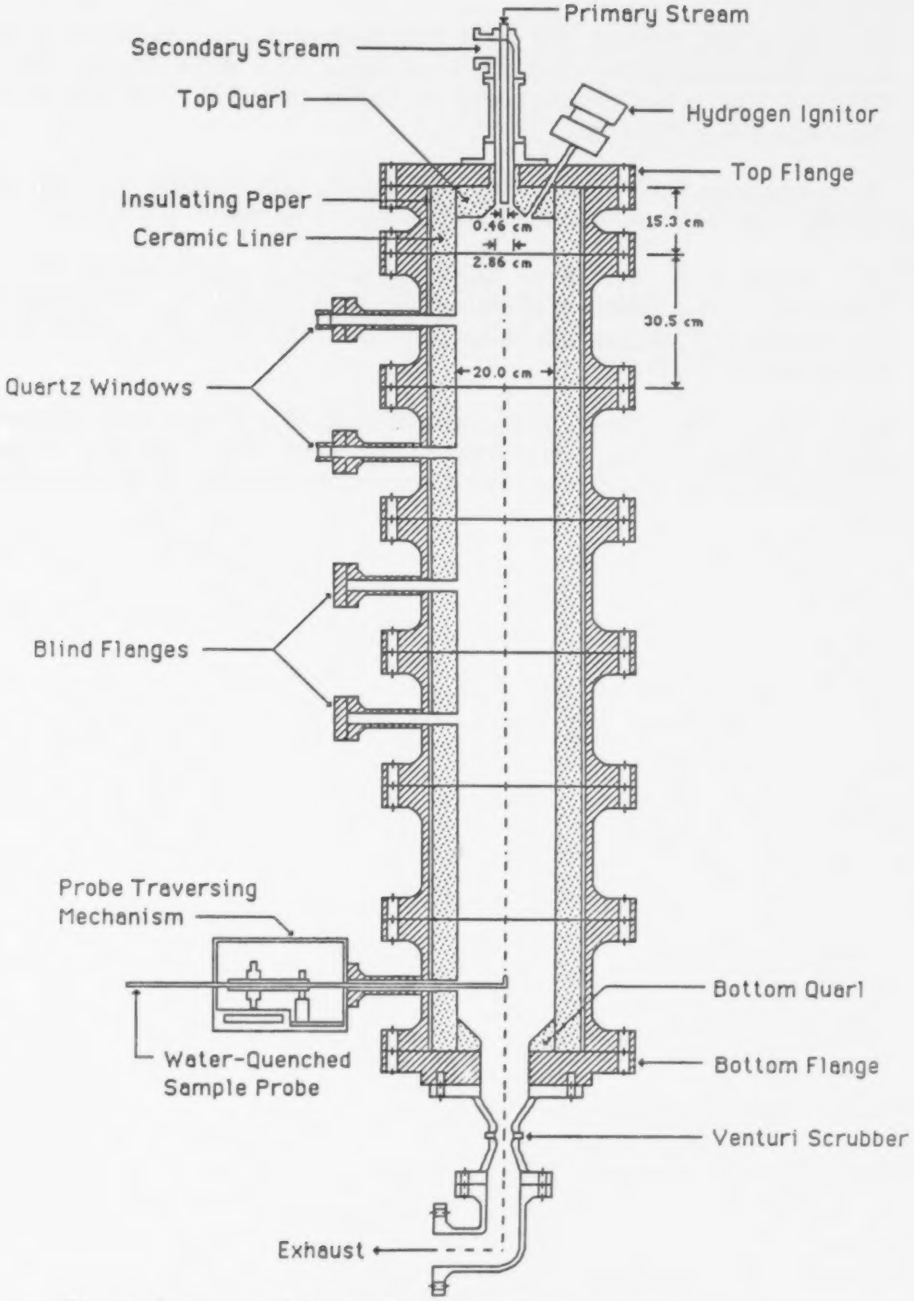


Figure 1. Schematic diagram of high-pressure entrained gasifier. [13]

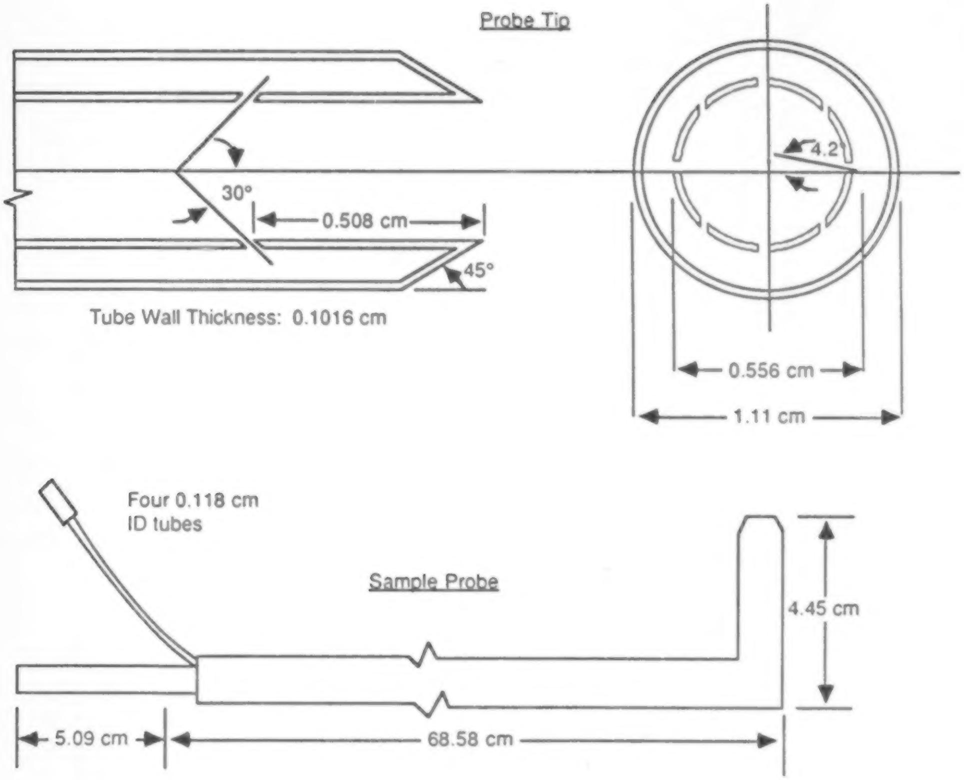


Figure 2. Schematic of traversing probe for gasifier.

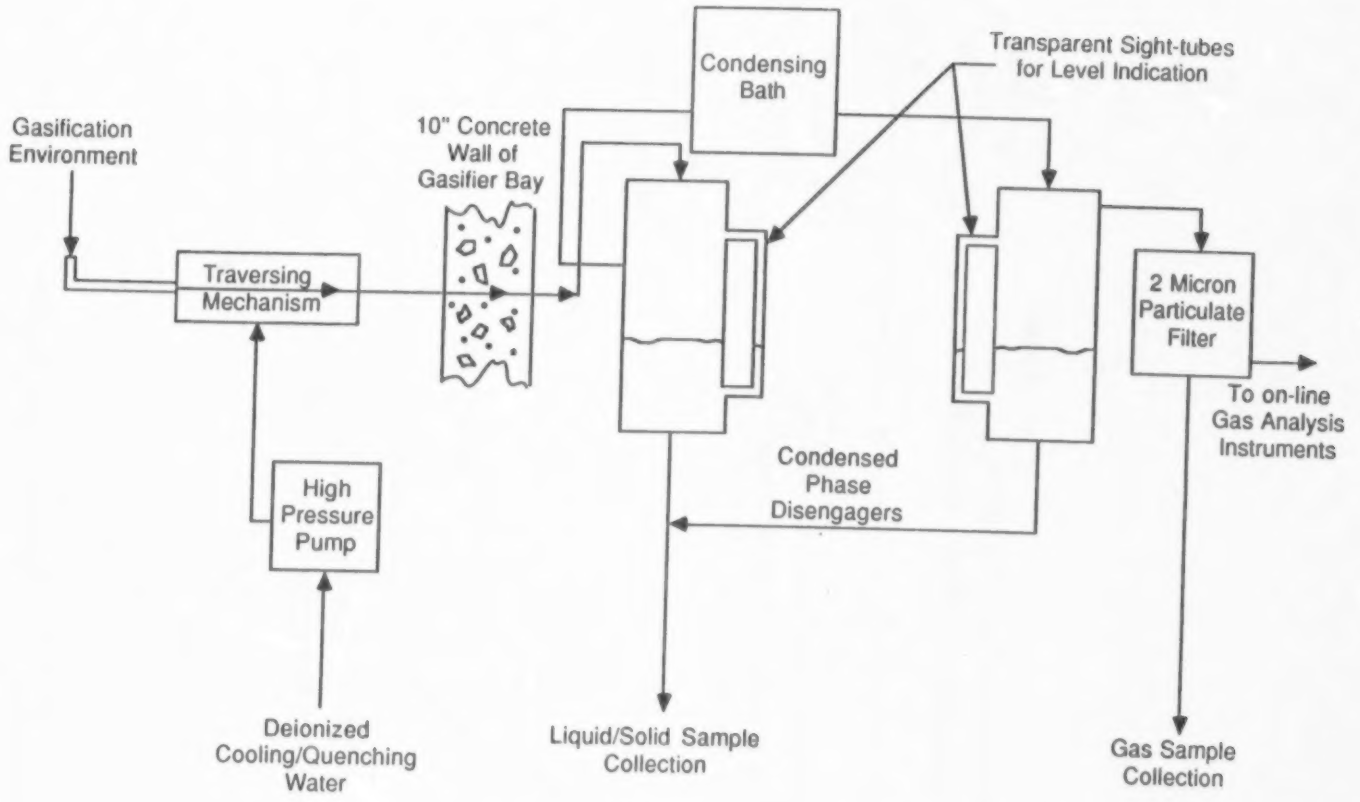

Gasification Environment
Traversing Mechanism
High Pressure Pump
Deionized Cooling/Quenching Water
10" Concrete Wall of Gasifier Bay
Condensing Bath
Transparent Sight-tubes for Level Indication
Condensed Phase Disengagers
Liquid/Solid Sample Collection
2 Micron Particulate Filter
To on-line Gas Analysis Instruments
Gas Sample Collection

Figure 3. Gasifier sample collection system.

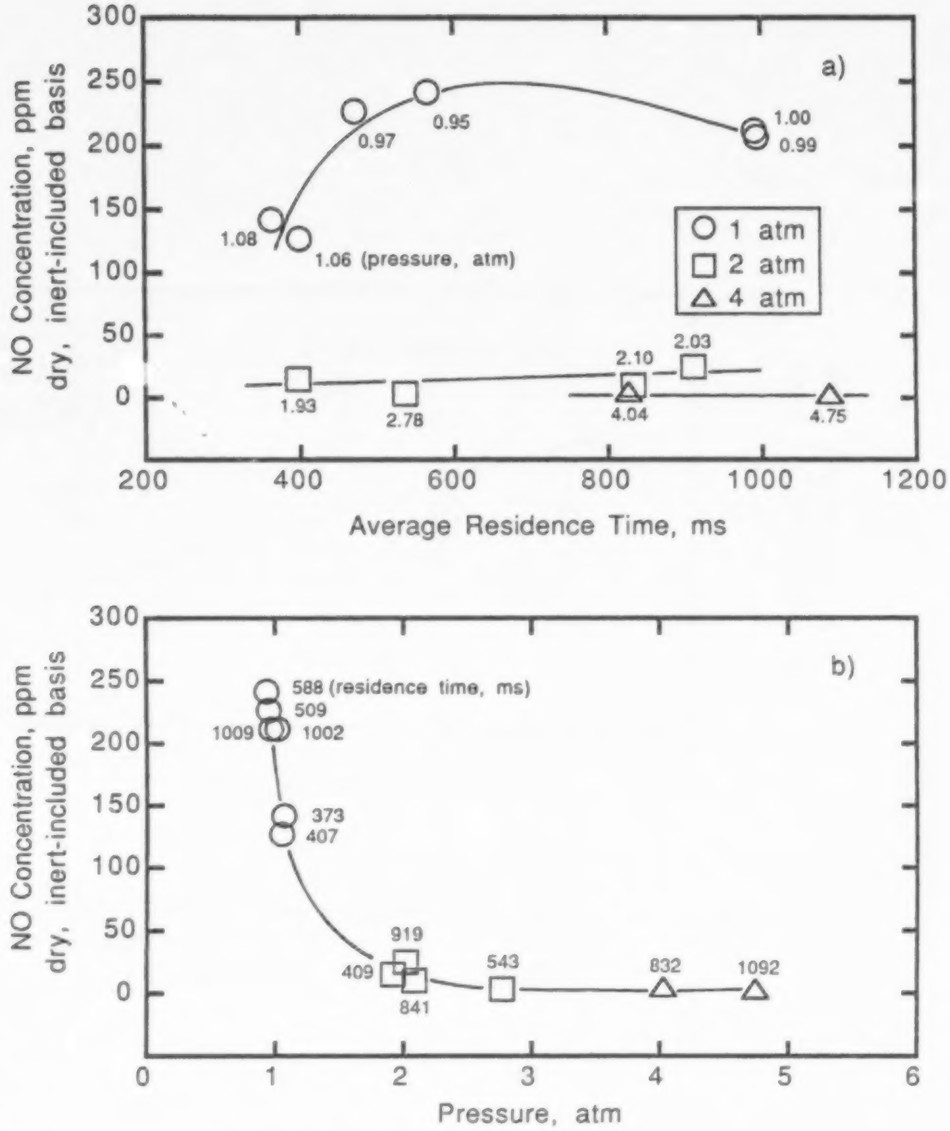


Figure 4. Influence of a) pressure and influence of b) residence time on effluent NO levels during gasification of Utah bituminous coal.

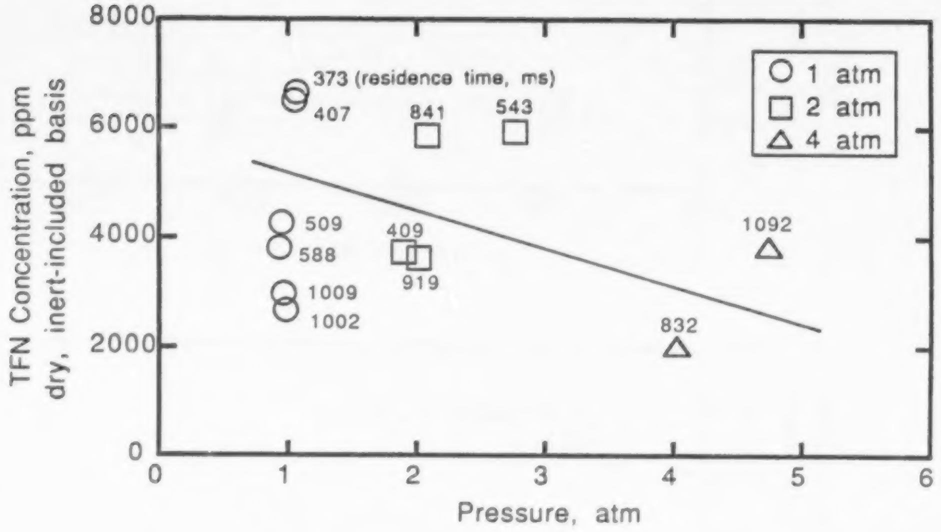


Figure 5. Influence of pressure and residence time on effluent TFN (HCN + NH_3 + NO) levels during gasification of Utah bituminous coal.

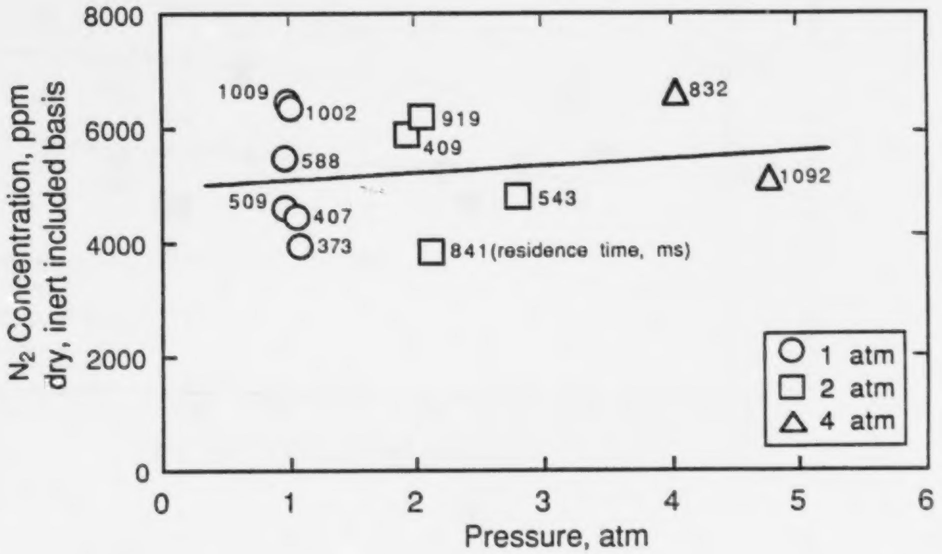


Figure 6. Influence of pressure and residence time on effluent N_2 levels during gasification of Utah bituminous coal.

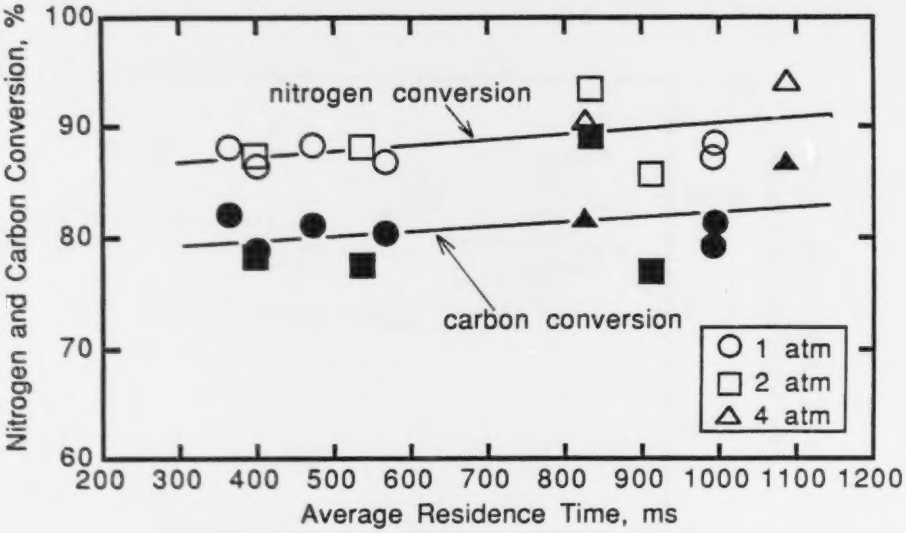


Figure 7. Effluent nitrogen and carbon conversion during gasification of Utah bituminous coal. Open symbols (○) denote nitrogen conversion, closed symbols (●) denote carbon conversion.

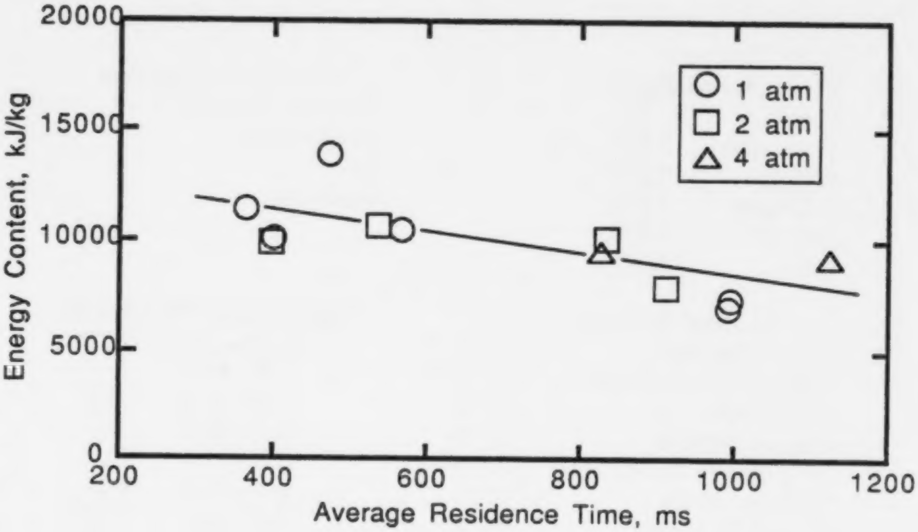


Figure 8. Calculated energy of product gas, in kJ per kg of wet product gas.

Table 1

Utah Coal Properties

Elemental Analysis

Carbon	71.8 %
Hydrogen	5.0 %
Oxygen	12.6 %
Nitrogen	1.5 %
Sulfur	0.4 %
Ash	8.5 %

Proximate Analysis

Volatile Content	42.2 %
Fixed Carbon	47.3 %
Ash	8.4 %
Moisture	2.4 %

Mineral Analysis

Silicon Dioxide	59.4 %
Aluminum Dioxide	17.0 %
Iron Oxide	3.7 %
Calcium Oxide	8.7 %
Magnesium Oxide	2.1 %
Sodium Oxide	1.1 %
Potassium Oxide	0.7 %
Titanium Dioxide	1.3 %
Phosphorus Pentoxide	0.6 %
Sulfur Trioxide	5.0 %

Ash Fusion Temperature, K

Initial	1491
Softening	1526
Hemispherical	1567
Fluid	1608

Particle Size Distribution

Range (μm)	wt. %
0.01 - 8.00	1.43
8.00 - 10.1	2.72
10.1 - 12.7	3.46
12.7 - 16.0	4.30
16.0 - 20.2	6.04
20.2 - 25.4	7.84
25.4 - 32.0	9.88
32.0 - 40.3	11.18
40.3 - 50.8	13.36
50.8 - 64.0	13.81
64.0 - 80.6	12.39
80.6 - 102	8.19
102 - 128	4.53
128 - 161	0.87

Mass Mean Diam., 48.7 μm

EVOLUTION AND REACTION OF FUEL NITROGEN DURING RAPID COAL PYROLYSIS AND COMBUSTION

Gregory J. Haussmann and Charles H. Kruger
High Temperature Gasdynamics Laboratory
Department of Mechanical Engineering
Stanford University
Stanford, CA 94305

ABSTRACT

The evolution and reaction of fuel nitrogen during the rapid pyrolysis and combustion of narrowly size-graded pulverized coal has been studied in an entrained flow reactor. Data are reported and interpreted for a 55 µm Montana Rosebud subbituminous coal and a 55 µm Pittsburgh Seam #8 (PSOC-1451) HVA bituminous coal. The pulverized coal is rapidly mixed into a high temperature gas stream, resulting in high heating rates (10^4-10^5 K/sec). Rapid pyrolysis is observed under these conditions, with pyrolysis times ranging from 11 msec at 1750K to 50 msec at 1300K. Pyrolysis products for both coals consist of CO, CO_2, light hydrocarbons, tar, and soot; nitrogen is released primarily in tar and as HCN. During pyrolysis, nitrogen is released in approximate proportion to carbon. Rapid combustion of most pyrolysis products occurs as they are released during fuel-lean single particle combustion studies with the Rosebud coal, with virtually no hydrocarbons, tar, or soot detected. During these dispersed particle oxidation studies, nitrogen is detected primarily as NO_x. This indicates that volatile nitrogen reduction to molecular nitrogen does not occur when such chemistry is confined to the thin volatile boundary layer surrounding individual particles. Pyrolysis studies using the Pittsburgh #8 coal reveal a significant tar yield, with most of the fuel-nitrogen released with the tar. The tar then either decomposes into gas-phase products (with nitrogen as HCN), or condenses into soot. At 1400K, 20% of the nitrogen released during pyrolysis is incorporated into soot. This portion of the volatile nitrogen is removed from participation in any nitrogen reduction chemistry which may be occurring, and thus may prove to be an important pathway for fuel nitrogen conversion to NO_x.

EXPERIMENTAL PROCEDURE

In the Stanford entrained-flow reactor (Fig. 1) narrowly size-graded pulverized coal is injected into a high temperature gas flow, which is generated by an argon arc-jet. This allows for the independent control of the gas temperature (1150 - 2000K) and the oxygen concentration (0 - 20%). This high temperature gas stream flows through an electrically heated test section with interior diameter 11.7 cm, at a velocity of 3 to 5 m/s. The Reynolds number based on diameter ranges from 1700 to 2000; in all cases the profiles of velocity and temperature are observed to be uniform both axially and radially, except for boundary layers near the reactor walls. Coal is supplied to the reactor from a fluidized-bed feeder, with particle densities ranging from 6 to 10 particles/cm^3. Particle are injected at the reactor centerline through a "sprinkler-head" nozzle, which injects particles at a 45° angle to the bulk flow. This results in rapid mixing, with a particle mixing time on the order of one msec. Residence times of up to 200 msec are achieved.

The extent of coal pyrolysis and combustion is investigated through the use of two classes of diagnostics: sampling gas-phase products and analysis of partly-reacted particles. Visual observation of reacting particles is also possible through two optical access ports. Gas and solid samples are collected by means of a single probe with multiple inlets, which can be traversed to sample at any location in the reactor. Gas-phase measurements include CO and CO_2 (non-dispersive infrared spectroscopy), light hydrocarbons (gas chromatography), oxygen (electrochemical analyzer), NO_x (chemiluminescent analyzer), NH_3, and HCN (ion-specific electrodes). The extent of reaction is determined by following the conversion of carbon into gas-phase products (CO, CO_2, and light hydrocarbons) and condensible pyrolysis products (tar and soot). Gas-phase measurements are possible starting at a residence time of 5 msec, with an estimated time resolution on the order of one msec.

Solid samples are collected through a quenching water spray. This technique is estimated to result in a quenching time of about one msec. The collected material contains partly reacted particles and condensable pyrolysis products (tar and soot). The tar/soot content of samples is determined through extraction in tetrahydrofuran (THF), with repeated washings and agitation in an ultrasonic bath. The THF/tar/soot mixture is decanted off and passed through an 0.2 μm Teflon filter, which has been found to trap soot particles, allowing the dissolved tar to pass through[1,2]. The tar is collected after room temperature evaporation of the THF. Micro-samples of partly reacted samples and the separated tar, soot, and char fractions are analyzed for C,H,N, and ash. Overall sample morphology is examined with a scanning electron microscope.

EXPERIMENTAL RESULTS AND DISCUSSION

Montana Rosebud Subbituminous

Experimental results for two coals are presented; Montana Rosebud subbituminous and Pittsburgh Seam #8 HVA Bituminous (PSOC-1451). The proximate and ultimate analyses of these coals are found in Table I. The overall pyrolysis and oxidation behavior of the Rosebud coal at a gas temperature of 1750K is seen in Figure 2. The rate and yield of pyrolysis is not significantly affected by the oxygen concentration, with 40% carbon conversion (corresponding to 55% DAF mass loss) reached at a residence time of 11 msec. Pyrolysis products consist of CO, CO_2, light hydrocarbons, tar, and soot. The light hydrocarbons evolved consist primarily of CH_4 and C_2 hydrocarbons, with a typical ratio of CH_4 / C_2's of 1 / 2.3 . Of the C_2 hydrocarbons released, C_2H_4 is the dominant species, with lesser amounts of C_2H_2, and very low levels of C_2H_6. The relative amounts of C_2H_2 / C_2H_4 / C_2H_6 detected range from 1 / 1.7 / 0.14 to 1 / 10 / 0.03 . The condensible pyrolysis product yield (tar plus soot), on a carbon basis, represents 35% of the total pyrolysis yield at 1750K. The initial tar yield may be significantly higher than this, since the released tar rapidly partitions into gaseous products and soot.

For the range of oxygen concentrations studied (2.0% - 15%), pyrolysis and oxidation of the pyrolysis products occur simultaneously at 1450K and 1750K, with all pyrolysis products oxidized to CO or CO_2 during pyrolysis. Under oxidizing conditions, condensible pyrolysis products and hydrocarbons are not detected in significant quantities at any time. This indicates either that tar combustion is rapid enough to prevent soot formation, or that soot oxidation is rapid as well. Fuel-nitrogen released during pyrolysis in an oxidizing environment is detected primarily as NO, with only low levels of HCN, NH_3, and tar/soot nitrogen detected. This high conversion of fuel-nitrogen to NO_x results from the fuel-lean conditions of the Rosebud studies (2.0% O_2 represents 300% excess air). At an oxygen concentration of 7.6%, nearly 100% of the original fuel-nitrogen is converted to NO_x, primarily as NO. This high level of NO_x formation for particles burning in a single particle combustion mode holds for gas temperatures ranging from 1150K to 1750K. In this dispersed burning mode, each particle is surrounded by an oxygen environment, confining nitrogen chemistry to a thin film surrounding each particle. Since the observed conversion to NO_x is virtually complete, only an insignificant amount of the volatile nitrogen has been reduced to N_2 within these films. This suggests that low NO_x conversion efficiencies can only be obtained when released volatile nitrogen species from individual particle clouds aggregate in regions which are deficient in oxygen, and rich in volatile nitrogen species.

Under oxidizing conditions, an abrupt decrease in the rate of carbon conversion is seen at the end of pyrolysis, as the transition between pyrolysis and char combustion occurs (Figure 2). The carbon conversion rates observed in the Stanford reactor during char combustion at 1750K are generally lower than the diffusion-limited rate[3]. The char oxidation rate at 2.0% O_2 is near the diffusion-limited rate, with a transition from zone III to zone II kinetics as the oxygen concentration rises from 2.0% to 15%. The overall combustion rates and burn-out times observed at 1750K are similar to those measured by Farzan and Essenhigh[4] in a high intensity vertical tunnel furnace, where rapid mixing was generated through impinging jet streams at the top of the furnace.

The DAF mass loss data for the present work is calculated from carbon conversion measurements by following the evolution of the major elements in the parent coal (C,H,O). Carbon is used as a tracer, with elemental analysis of the tar, soot, and char fractions allowing a determination of the amount of hydrogen, oxygen, and nitrogen in each. Thus the percent release from the parent coal of each component is known, and the corresponding DAF mass loss can be calculated. The correlation between carbon conversion and DAF mass loss (Figure 3) reflects the initial loss of oxygen and hydrogen at a faster rate than carbon.

The correlations for pyrolysis carbon, nitrogen, hydrogen, and oxygen loss vs. DAF mass loss are plotted in Figure 4, representing gas temperatures ranging from 1300K to 1750K. The rapid loss of oxygen at low mass loss levels indicates that oxygen containing functional groups, such as relatively loosely bound carboxyl groups, are leaving early during pyrolysis. This observation is in general agreement with the work of Serio et al[5], where the functional group composition of Montana Rosebud subbituminous was reported. Approximately half of the original oxygen was reported as CO_2 (presumably as carboxyl groups, –COOH), with the remainder in ether groups (–C–O–*), primarily as "loose ether". These oxygen-rich functional groups would be expected to evolve early during pyrolysis, resulting in the disproportionate loss of oxygen at early times. The loss of oxygen and hydrogen vs DAF mass loss is almost identical, with nearly complete oxygen and hydrogen loss during the devolatilization phase.

The evolution of fuel nitrogen during pyrolysis is fundamentally different from that of oxygen and hydrogen, as seen in figure 4. A substantial delay exists between the initiation of mass loss and the evolution of fuel nitrogen. A linear least-squares fit to the data has an x-intercept of 24% DAF mass loss. After this period of no nitrogen release, the fractional loss of nitrogen is higher than that of mass, with a curve fit slope of 1.36. This observation is consistent with the hypothesis of a significant induction period during which essentially no fuel-bound nitrogen is released. Such an induction period is thought to result from the relatively stable ring structures such as pyridines and pyrroles (C_5N and C_4N rings) that comprise fuel-nitrogen[6]. During this induction period, pyrolysis products evolve primarily through the elimination of peripheral groups. It is only later in pyrolysis when significant bridge dissociation has occurred (and perhaps some ring rupture), that fuel-bound nitrogen is released, either in tar or as HCN. The delay between the onset of mass loss and the onset of nitrogen loss, as well as the higher fractional rate of nitrogen vs. mass loss, is similar to results obtained by Pohl and Sarofim[7]. They also observed an induction period with no nitrogen loss, followed by nitrogen release with a ratio of fractional nitrogen vs mass loss of 1.25 for a lignite coal, and 1.5 for a bituminous coal.

Nitrogen Loss Correlation.

A simple first-order kinetics model has been applied to the evolution of fuel nitrogen from the Rosebud coal. The model is outlined below.

$$dB/dt = -A \exp[-E_a/RT_p(t)]\, B(t) \qquad (1)$$

where:

$B(t)$ = $[N_\infty - N(t)]/N_\infty$
N_∞ = Ultimate Nitrogen Loss
E_a = Effective activation energy
A = Pre-exponential constant
$T_p(t)$ = Particle temperature

To obtain the particle temperature as a function of residence time in the reactor, a simple heat balance is performed, as below.

$$Q'' = \text{heat flux to particle} = h(T_p - T_\infty) - \varepsilon_w \sigma T_w^4 + \varepsilon \sigma T_p^4 \qquad (2a)$$

$$(4\pi r_p^2)Q'' = m_p C_p (dT_p)/(dt) \qquad (2b)$$

The parameters, and important assumptions, are below:

m_p = particle mass, determined vs. time from experimental results
T_g = Gas temperature
Nu = $hd/k_g = 2 + 0.3Pr^{1/3}Re^{0.6}$ (Note: Re decays rapidly after injection)
k_g = Thermal conductivity of argon at $T_{film} = (T_{gas} + T_p)/2$
ε_w = wall emissivity, ~ 1
ε_p = particle emissivity, ~ 1
ΔH_{rxn} = pyrolysis heat of reaction, ~ 0
C_p = Particle heat capacity, an increasing function of temperature[8]

- Internal temperature gradients are small
- Stefan flow negligible

Equation (2b) is solved to give the particle temperature vs. residence time, and this data is input into a computer model to calculate B(t) through numerical integration of eqn. (1). A least-squares best fit for values of A and E_a for the data obtained in the Stanford entrained-flow reactor can then be calculated. This transient temperature model for the particle temperature and nitrogen evolution yields best-fit values of $E_a = 22$ kcal/mole, and $A = 1.15 \times 10^6$. The results of this calculation for three gas temperatures can be seen in Fig. 5, where the value of B has been plotted vs. the transient particle temperature. It can be seen that the evolution of fuel nitrogen occurs during the particle heating stage, and that most nitrogen evolution occurs well before the particle temperature reaches the gas temperature. The difference between the particle temperature and the gas temperature when the loss of nitrogen reaches 50% of its ultimate value is: 90K at a gas temperature of 1300K, 240K at 1500K, and 390K at 1750K. While at the lower temperatures of many pyrolysis experiments an understanding of the particle temperature as a function of time may not be as crucial in evaluating the kinetics ofnitrogen evolution, at gas temperatures and heating rates typical of pulverized coal combustion ($\sim 10^5$ K/sec)[9], the particle temperature history must be considered.

Pittsburgh Seam #8 HVA Bituminous

Recent experimental work in the Stanford entrained-flow reactor has focused on pyrolysis studies of 55 μm Pittsburgh Seam #8 HVA bituminous coal. The overall pyrolysis DAF mass loss for the Pittsburgh coal at 1400K is seen in Figure 6. Pyrolysis is essentially complete at a residence time of about 20 msec, reaching a DAF mass loss of 40%, with the distribution of pyrolysis products continuing to shift until about 50 msec. The Pittsburgh #8 coal yields a significant amount of tar as the primary pyrolysis product, with the initial gas-phase pyrolysis yield fairly low. This is consistent with the results of Ballantyne et al[10], where secondary reactions were eliminated through laser heating in a cold gas. Under the conditions of their experiment, Pittsburgh #8 coal was found to release only low levels of gaseous volatiles for particle temperatures up to 2100K at a residence time of 30 msec. The current experiment reveals a significant initial yield of tar (Figure 6), with secondary decomposition reactions and soot formation occurring simultaneously in the hot gas environment. The tar yield drops off rapidly from a peak at the end of pyrolysis (20 msec), with virtually no tar present at 50 msec. On a DAF mass basis, 60% of the tar present at 20 msec is converted to gas-phase products, and 40% to soot. The strong propensity of the tars evolved during the pyrolysis of pulverized coals to form soot has been noted by several researchers[1,2,11], although only limited data exists as to the yield and nature of the soot produced. The pyrolysis product distribution can be broken up further on a carbon basis, as seen in Figure 7. Gas-phase carbon containing species consist primarily of CO and CO_2, with only a few-percent of light hydrocarbons present. About 11% of the original coal carbon is ultimately converted into soot, representing about 30% of the total carbon released during pyrolysis.

Size distributions of partly-reacted samples measured with a Coulter-counter® are seen in Figure 8, for the raw coal and for samples devolatilized at 1400K, collected at various residence times. The solid curves represent the entire collected sample (char+tar+soot), while the dotted curves represent the THF-insoluble fraction, i.e. char. As time goes on a significant peak at about 5 microns is observed to develop in the whole sample size distribution, coinciding with the soot formation seen in Figure 7. The size-distributions for the two sample fractions are nearly identical, with the peak near 5 microns not present in the char fraction. Thus this peak is due to the soot/tar fraction of the partly-reacted sample. Tar released during the pyrolysis of pulverized coal has been found to condense primarily (~90%) onto the soot particles[1]. This peak at a particle diameter of 5 microns represents a large number of individual soot particles cemented together by tar. Scanning electron micrographs of the soot fraction show an agglomeration, with no identifiable structures down a size of about 0.5 microns (5000 Å), the resolution of the instrument used. Nenninger[1], in a study of the aerosols generated during coal pyrolysis in an entrained-flow reactor, found primary soot particles ranging in size from 140 - 360 Å.

The evolution of fuel-nitrogen is of particular interest, as the distribution of fuel-nitrogen into the tar, soot, and gas fractions are not well understood. This distribution is represented in Figure 9, for 1400K pyrolysis of the Pittsburgh coal. Preliminary results from ion-specific electrode analysis of the product gases indicate that HCN is the dominant nitrogen containing gas released, with only low levels of NH_3 detected. The initial tar released contains a significant fraction of the evolved fuel nitrogen. Tar nitrogen has been found to be bound in the same ring structures as in the parent coal[12], and thus is expected to be in relatively stable pyridine and pyrrole structures. The majority of gas-phase nitrogen containing species result from secondary reaction of the released tar . A significant portion of the fuel nitrogen, however, is incorporated into the soot fraction, with about 7% of the original fuel-nitrogen converted into soot. This represents 22% of the total fuel-nitrogen released during pyrolysis ("volatile nitrogen"). Soot nitrogen appears to be relatively stable, with essentially no loss of nitrogen from the soot fraction occurring from 50 msec to 120 msec.

SUMMARY AND CONCLUSIONS

The evolution and reaction of fuel nitrogen has been measured during the rapid pyrolysis and combustion of pulverized Montana Rosebud subbituminous and Pittsburgh Seam #8 HVA bituminous coals. The Rosebud coal exhibits rapid hydrogen and oxygen loss at high heating rates (10^4-10^5 K/sec), with virtually complete loss of these elements during pyrolysis. A substantial delay exists between the onset of mass loss and the onset of nitrogen evolution, representing a significant induction period during which essentially no nitrogen loss occurs. This is thought to result from the relatively thermally stable ring structures in which fuel nitrogen is contained. During this induction period, pyrolysis products result primarily from the elimination of peripheral groups (carboxyl, ether, methyl, etc.). It is only later in pyrolysis, after significant bridge dissociation has occurred (and perhaps some ring rupture), that fuel nitrogen is released, either in tar or as HCN.

A first order kinetics correlation for the evolution of fuel nitrogen has been applied to the Rosebud data, coupled with a model for the transient particle temperature. The best fit parameters for nitrogen loss during pyrolysis at gas temperatures ranging from 1300K to 1750K are an activation energy of 22 kcal/mole, and a pre-exponential factor of 1.15×10^6 sec^{-1}. The rapid mixing of coal particles into the hot gas stream in the current work produces higher heating rates than for the same gas temperature in facilities with less rapid mixing. As the heating rate is increased, the temperature range over which most nitrogen loss occurs widens and also moves farther from the bulk gas temperature. In order to compare kinetic parameters from disparate experiments, an accurate representation of the particle temperature during pyrolysis is essential.

Pyrolysis and oxidation of the pyrolysis products occur virtually simultaneously during single particle combustion of Rosebud coal for oxygen concentrations ranging from 2.0% to 15%. Complete conversion of fuel nitrogen to NO_x is seen under oxidizing conditions for gas temperatures ranging from 1150K to 1750K. Since each coal particle is surrounded by an oxygen environment in this dispersed particle experiment, nitrogen reduction chemistry is confined to a thin film surrounding each particle. Under such conditions in the Stanford reactor, only an insignificant amount of the volatile nitrogen is converted to N_2 in these films, indicating that low overall NO_x conversion efficiencies can only be obtained when volatile nitrogen species from individual particle clouds can aggregate in regions which are oxygen poor, and rich in volatile nitrogen species.

The primary product released during the pyrolysis of a Pittsburgh Seam #8 HVA bituminous coal is tar, which in the hot gas phase rapidly partitions either into gaseous products, or into soot. This partitioning of tar into gaseous products and soot occurs quickly, and is complete by a residence time of 50 msec at 1400K. During pyrolysis at 1400K, 20% of the volatile nitrogen is incorporated into the soot fraction. Soot nitrogen is stable at this temperature, with no loss of nitrogen from the soot observed. This portion of the volatile nitrogen is removed from any nitrogen reduction chemistry which is occurring in the gas phase, and may prove to be a significant factor in the overall pathways by which fuel nitrogen is ultimately converted into NO_x.

ACKNOWLEDGMENT

This work has been supported by the Electric Power Research Institute through Grant # RP 8005-2, under the direction of Dr. George Offen.

REFERENCES

1. R.D. Nenninger, "Aerosols Produced from Coal Pyrolysis", Sc.D. Thesis, M.I.T. (1986).

2. M.J. Wornat, A.F. Sarofim, J.P. Longwell, "Pyrolysis Induced Changes in the Ring Number Composition of Polycyclic Aromatic Compounds from a High Volatile Bituminous Coal", 22nd Symposium (International) on Combustion, The Combustion Institute, 1989.

3. G.J. Haussmann and C.H. Kruger, "Rapid Pyrolysis and Combustion of Pulverized Montana Rosebud Subbituminous Coal", 22nd Symposium (International) on Combustion, The Combustion Institute, 1989.

4. H. Farzan and R.H. Essenhigh, "High Intensity Combustion of Coal", 19th Symposium (International) on Combustion, p. 1105-1111, The Combustion Institute, 1982.

5. M.A. Serio, D.G. Hamblen, J.R. Markham, and P.R. Solomon, "Kinetics of Volatile Product Evolution in Coal Pyrolysis: Experiment and Theory", Journal of Energy and Fuels, Vol. 1, 1987, pp. 138-152.

6. P.R. Solomon and M.B. Colket, "Evolution of Fuel Nitrogen in Coal Devolatilization", Fuel, Vol. 57, December 1978, pp. 749-755.

7. J.H. Pohl and A.F. Sarofim, "Devolatilization and Oxidation of Coal Nitrogen", 16th Symposium (International) on Combustion, The Combustion Institute, 1976, pp. 491-501

8. D. Merrick, "Mathematical Models of the Thermal Decomposition of Coal: 2. Specific Heats and Heats of Reaction", Fuel, Vol. 62, May 1983, pp. 540-546.

9. J.D. Freihaut, W.M. Proscia, and D.J. Seery, "Fuel Bound Nitrogen Evolution During the Devolatilization and Pyrolysis of Coals of Varying Rank", Presented at the 1987 Joint Symposium on Stationary Combustion NO_x Control, New Orleans, LA.

10. A. Ballantyne, H. Chou, K. Neoh, N. Orozco, and D. Stickler, "Cold Atmospheric Pyrolysis of Pulverized Coal Using 10.6 µm Laser Heating", Presented at the American Chemical Society New York City National Meeting, 1985.

11. W.J. McClean, D.R. Hardesty, and J.H. Pohl, "Direct Observations of Devolatilizaing Pulverized Coal Particles in a Combustion Environment", 18th Symposium (International) on Combustion, The Combustion Institute, 1981, pp. 1239-1248.

12. J.D. Freihaut, M.F. Zabielski, and D.J. Seery, "A Parametric Investigation of Tar Release in Coal Devolatilization", 19th Symposium (International) on Combustion, The Combustion Institute, 1982, pp. 1159-1167.

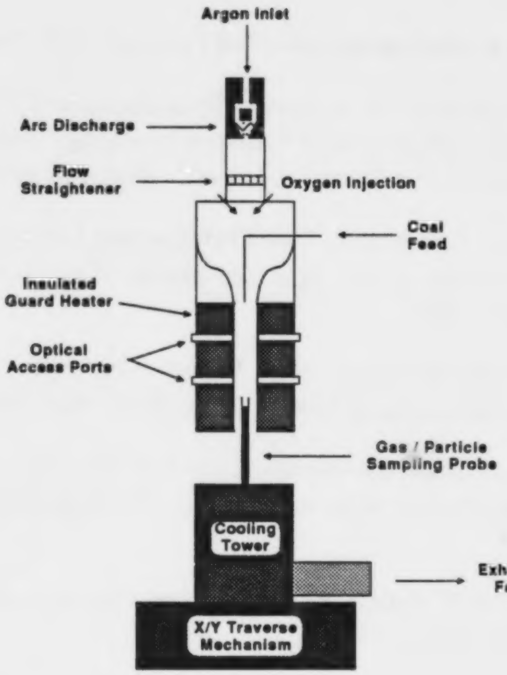


Figure 1. Stanford Entrained-Flow Reactor.

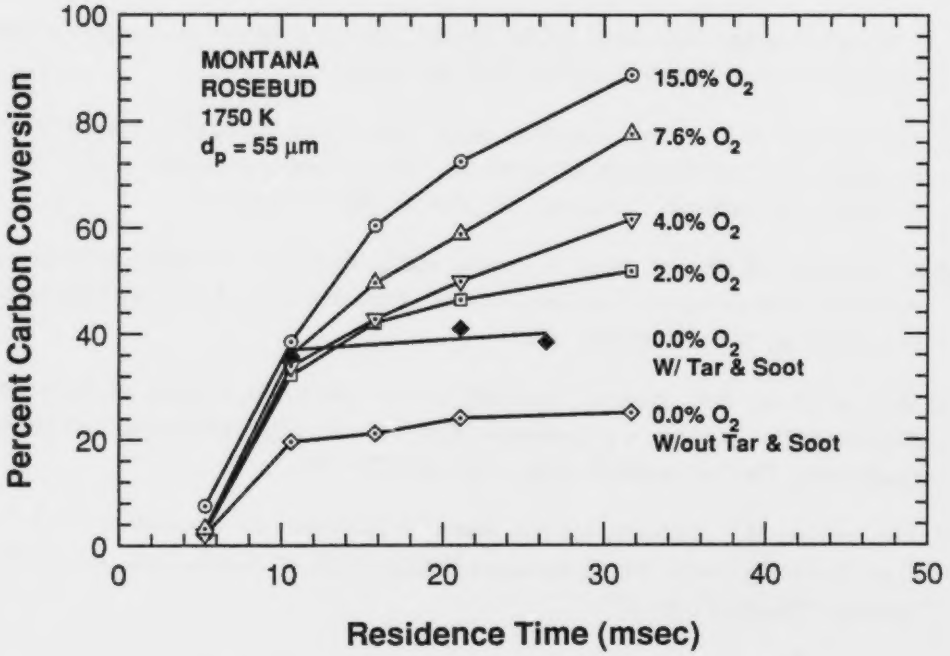


Figure 2. Rosebud Carbon Conversion vs Residence Time.

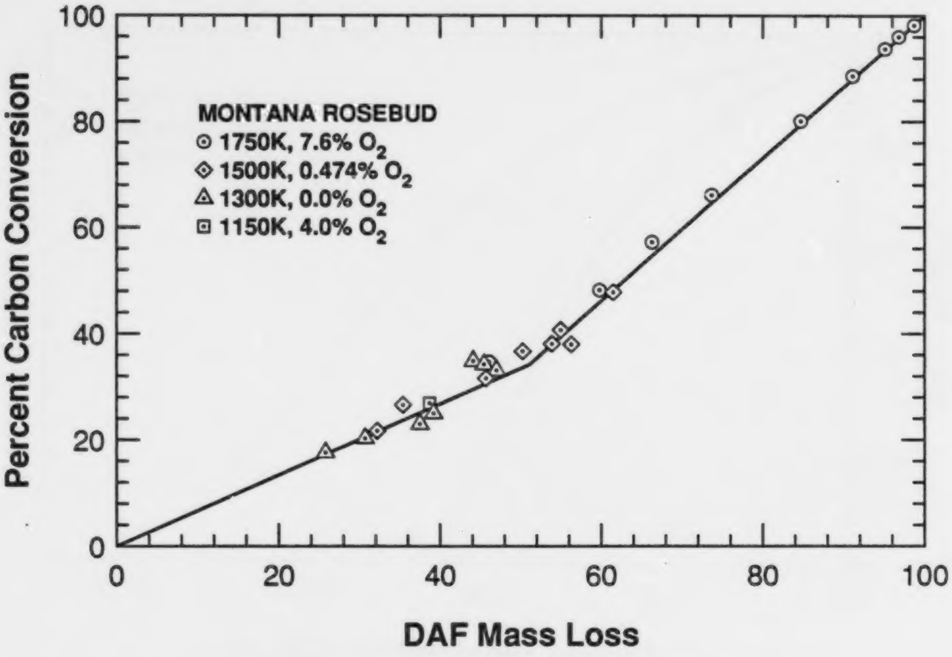


Figure 3. Rosebud Carbon Conversion vs DAF Mass Loss.

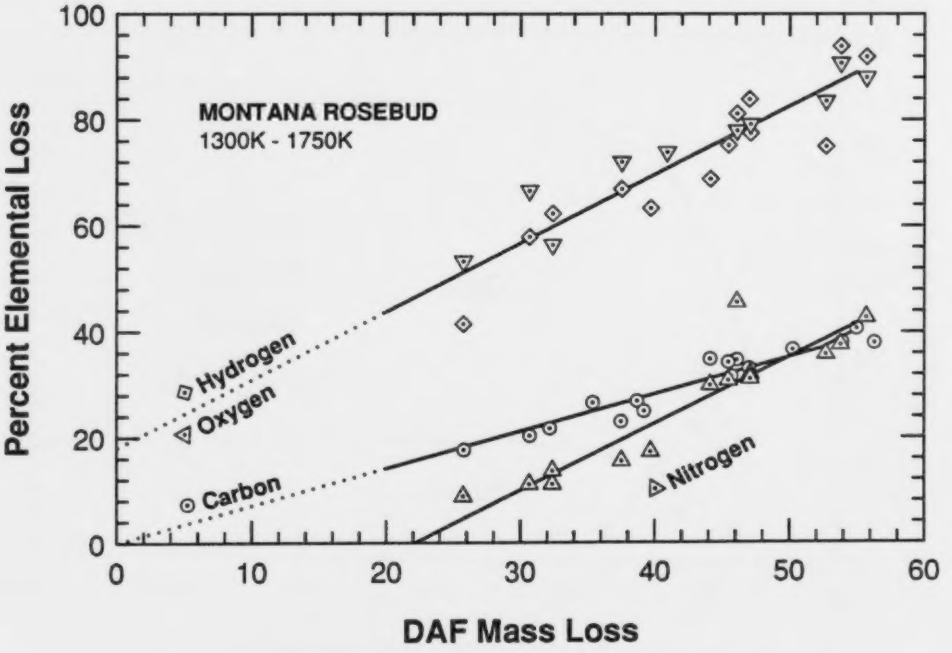


Figure 4. Rosebud Pyrolysis Elemental Loss vs DAF Mass Loss.

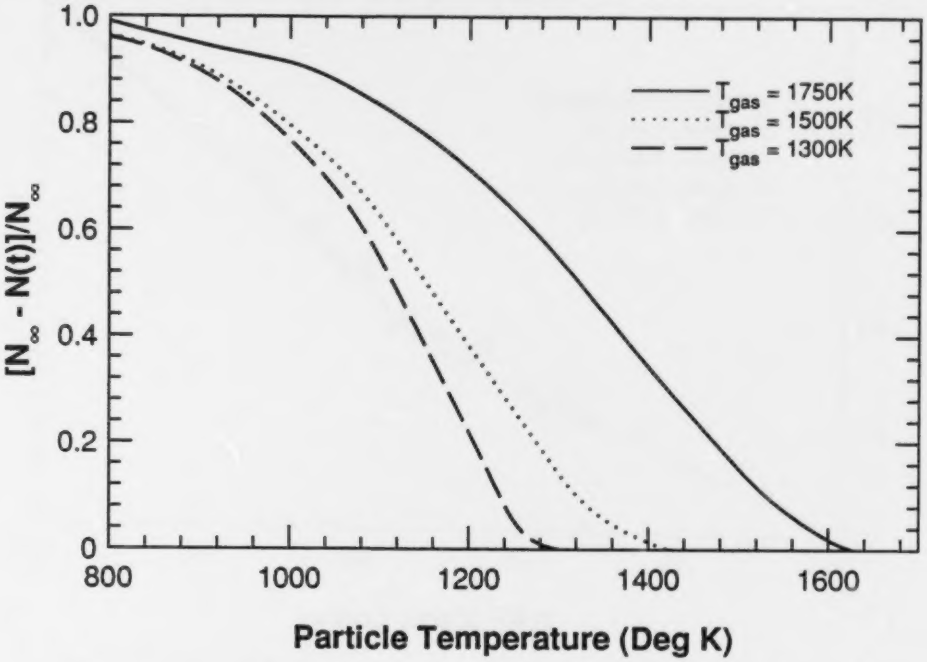


Figure 5. Rosebud Pyrolysis Nitrogen Loss vs Transient Particle Temperature.

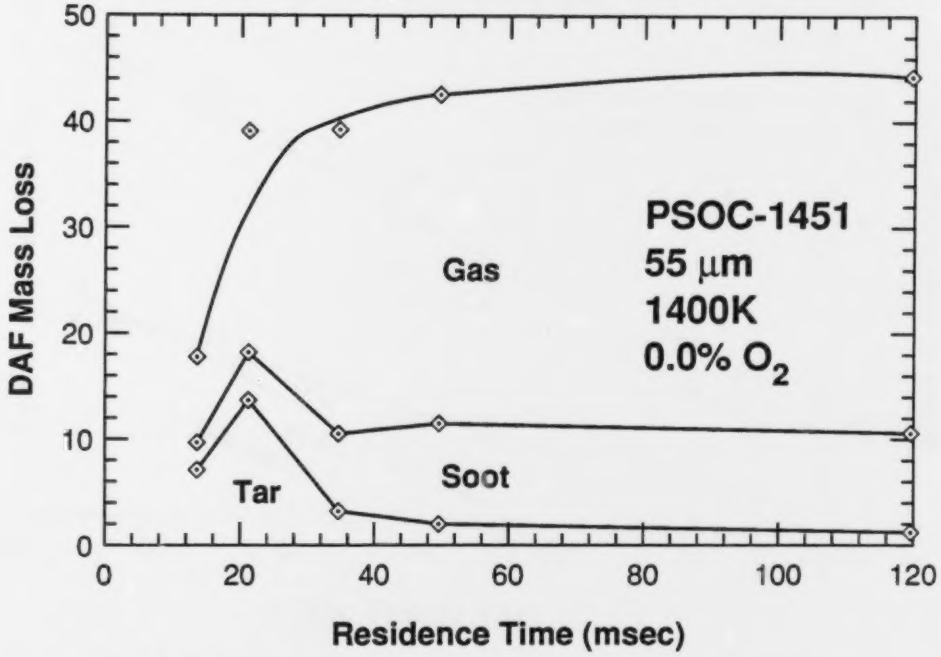


Figure 6. Pittsburgh #8 Pyrolysis DAF Mass Loss vs Residence Time.

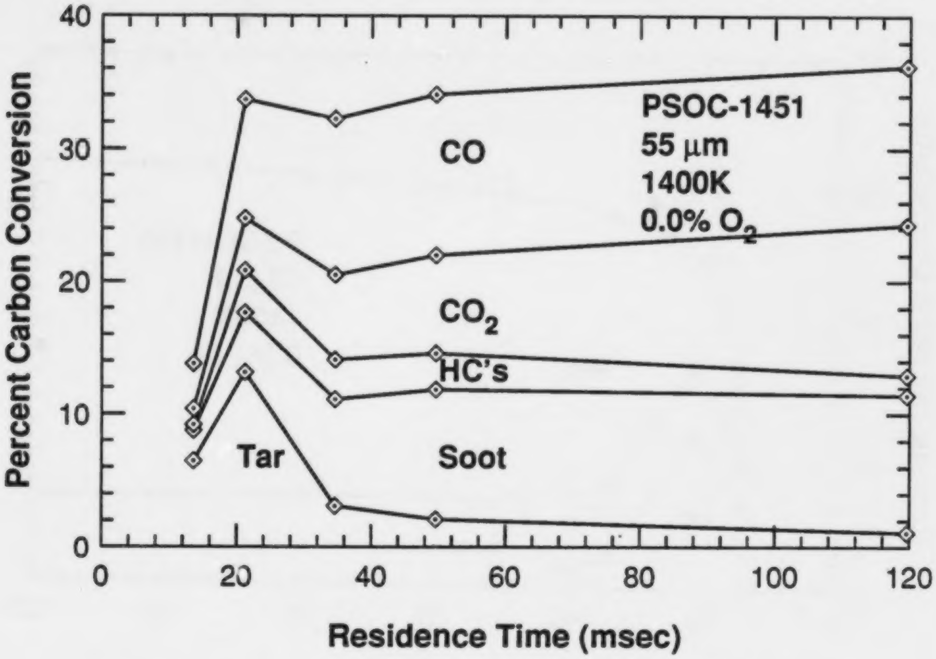


Figure 7. PSOC-1451 Pyrolysis Carbon Conversion vs Residence Time

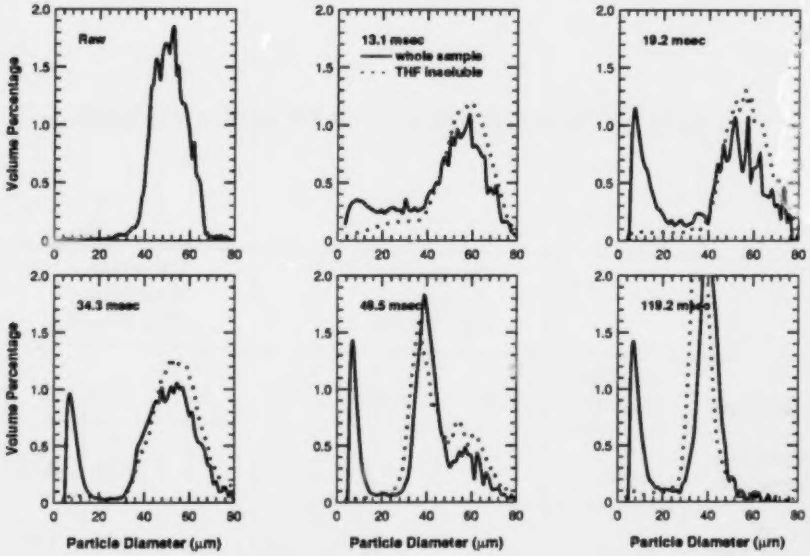


Figure 8. Pittsburgh #8 Char Size Distributions vs Residence Time.

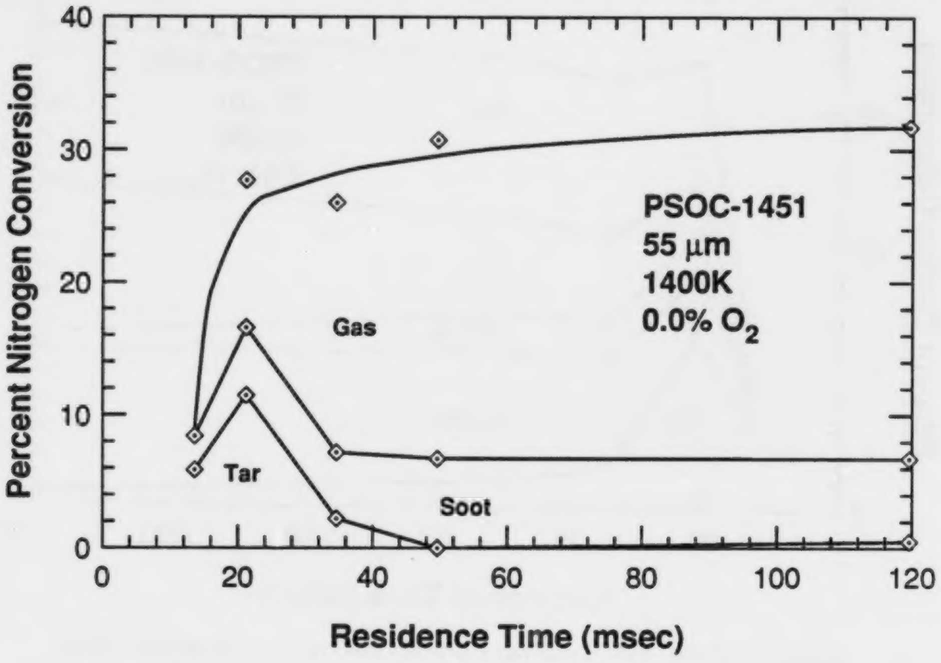


Figure 9. Pittsburgh #8 Pyrolysis Nitrogen Conversion vs Residence Time.

TABLE I - PROXIMATE AND ULTIMATE ANALYSES.

		Proximate Analysis Dry Wt. %		Ultimate Analysis Dry Wt. %				
Coal Type	BTU/lb (moist)	V.M.	ASH	C	H	N	S	O
Montana Rosebud	10186	42.4	10.1	67.2	4.5	0.78	0.52	17.7
Pitt. #8 PSOC-1451	14342	-----	3.34	81.5	5.5	1.71	1.02	6.93

THE EFFECT OF PROCESS VARIABLES ON NOx AND NITROGEN SPECIES REDUCTION IN COAL FUEL STAGING

K J Knill and M E Morgan
International Flame Research Foundation
P O Box 10.000, 1970 CA IJmuiden
the Netherlands

ABSTRACT

An investigation of the effect of process variables on NOx reduction in the coal reburning zone was undertaken to resolve discrepancies noted in the literature. High volatile bituminous coals were injected into a turbulent isothermal reactor simulating a coal reburning zone. The change in NOx, HCN and NH_3 concentrations were measured over a wide range of process conditions.

The NOx concentration could be reduced from 200-600 ppm to less than 50 ppm under optimum conditions. Reburn fuel fraction, primary stoichiometry, temperature and residence time were interdependent and significant parameters. However, inlet NOx concentration, coal type and particle size were not significant at optimum conditions. Reductions in NOx and HCN were accurately predicted by a published model. The results provide insight into the processes occurring in the reburning zone and guidelines for applying the results to furnace design are proposed.

INTRODUCTION

Fuel staging or "reburning" has been shown to be an effective method of NOx emission reduction [1 - 3]. Reburning involves injecting fuel into a secondary combustion zone downstream of the primary combustion zone. The reburning zone is operated sub-stoichiometrically in order that hydrocarbon radicals from the reburning fuel may reduce NO formed in the primary zone according to the reaction:

$$CH_i + NO \rightarrow HCN + O \qquad (R1)$$

Once the HCN has been formed, it may be reduced through NCO and NH_i to molecular nitrogen according to the simplified scheme shown in Figure 1. This process occurs rapidly in combustion environments with characteristic reduction times of approximately 50 ms [4 - 6].

The variables of primary importance in fuel staging have been identified as:

i) Reburning fuel type: Several studies suggest that hydrocarbon gas is a more effective reburning fuel than coal [7 - 11]. However, there is no general agreement regarding the effectiveness of coal as a reburning fuel.

ii) Reburn fuel fraction: Sufficient hydrocarbon radicals must be available to reduce NOx, but the quantity of coal required to produce the radicals is not known.

iii) Reburn zone stoichiometry: Sufficient oxygen must be available to convert HCN (formed during hydrocarbon radical reaction with NO) to NCO. The optimum reburning zone stoichiometry appears to be 0.65 to 0.95.

iv) Reburn zone residence time: A residence time greater than 400 ms is required to reduce HCN to N_2 before tertiary air injection. Some studies had concluded that residence times as long as 1 s may be necessary. In certain applications, this parameter may dictate the fuel staging configuration of the furnace.

v) Reburn zone temperature: It has been shown that gas fuel staging reactions are favoured at temperature greater than 1200°C. This is attributed to an increase in the rate of the NO/CH_i and HCN/O reactions. The effect of temperature on coal reburning effectiveness has not been resolved. It has been shown that, for some coals, lower temperature may improve coal reburning effectiveness due to the reaction of NH_3 in the coal with NOx.

vi) Mixing: Mixing between primary NOx and reburning fuel must be rapid and intense in order to minimize NOx emissions. Greater mixing may be attained by increasing the reburn fuel injection momentum with additional secondary fuel transport air. This may lead to early oxidation of reburning fuel hydrocarbon volatiles, thereby reducing fuel staging effectiveness.

vii) Fuel nitrogen content: Reburning fuels containing nitrogen may have limited effectiveness in reducing NO emissions if the primary zone NOx level is less than 150 ppm. However, this laboratory scale observation has been refuted at the utility boiler scale.

viii) Fuel reactivity: Coals with a higher volatile matter content and higher char reactivity appear to be more effective reburning fuels. The higher volatile matter content may result in a higher fraction of CH_i radicals necessary to reduce NOx. Highly reactive chars will require lower burnout times in the tertiary combustion zone, but this has not been studied extensively in the literature.

A fundamental investigation of the processes occurring in the coal fired, fuel staging zone was undertaken as a result of the uncertainties noted from the literature. In this report, the results of a parametric study to determine the most important variables in coal fuel staging are described. The change in NOx, HCN and NH_3 concentrations in the reburning zone, measured over a wide range of process conditions, was used to describe the optimum process conditions for coal fuel staging. Nitrogen species reduction was predicted using a published model.

METHOD

The trial was conducted using the isothermal plug flow reactor (IPFR) illustrated in Figure 2. The reburning zone was produced by injecting coal into a preheated gas stream which simulated primary zone coal combustion products. The preheated gas was produced by burning natural gas in a mixture of air and nitrogen. The nitrogen was added to moderate the gas temperature leaving the precombustor. The gas composition along the reactor length could be measured to determine the concentrations of NOx, HCN and NH_3. The effect of the process variables, identified in the introduction, on reburning effectiveness was tested.

Three bituminous coals were selected for this investigation and their ultimate and proximate analyses are shown in Table 1. Bituminous coals were selected to study the effect of volatile matter content on NOx reduction for coals of the same rank.

The coals had volatile matter contents ranging from 25% to 42% DAF. These coals were air dried and pulverized to three particle size ranges: normal (75% < 75 μm); fine (93% < 75 μm); and micronized (100% < 40 μm).

The isothermal plug flow reactor consists of three sections: gas preheater, main reactor and product collector. The gas preheater is a 30 cm diameter by 1 m long refractory lined cylinder with a swirled gas burner at one end and a T-piece and chimney at the other end. The IPFR main reactor consisted of a 117 mm ID by 2 or 5 m long alumina tube heated externally by graphite heating elements. The reactor was connected to the preheater T-piece by a ceramic venturi. The preheated gas flowed into the reactor through the venturi where it mixed rapidly with the coal, injected through a water cooled feeder probe. A small amount of NO was added to the transport gas in the feeder probe to obtain a predetermined NOx concentration. The gas flowed out of the reactor through an aspirator and exhausted to vent.

Collection probes could be inserted into the reactor from the bottom. The NOx, CO, CO_2 and O_2 concentrations were measured using a steam heated probe. The HCN and NH_3 concentrations were measured using the IFRF HCN probe, described elsewhere [12]. The analysis of HCN and NH_3 were performed according to NEN 6489 and NEN 6472/6644 standards for measurement in waste water.

A Box-Behnkin experimental design [13] was used to determine the simultaneous effect of the process variables on NOx, HCN and NH_3 concentrations. Each process variable was studied at three levels in order to construct a response surface curve. The conditions were:

1. coal type:	Obed Mountain, Scotts Branch, Hugo
2. particle size:	normal, fine, micronized
3. reburn fuel fraction:	10, 20, 30%
4. primary stoichiometry:	1.0, 1.075, 1.15
5. reburn temperature:	1100, 1250, 1400°C
6. primary NOx concentration:	200, 400, 600 ppm
7. reburn residence time:	0.1, 0.3, 1.0 s

RESULTS AND DISCUSSION

The effect of process variables on coal reburning were measured in 59 experimental tests. Each test was conducted twice: once to measure NOx, CO, CO_2 and O_2 concentrations and once to measure the HCN and NH_3 concentrations. During the HCN and NH_3 samples, a probe located at the bottom of the reactor was used to measure the NOx concentration to ensure repeatability.

Evolution of N-species from the Coals

The formation of N-species from the fine grind fractions of the three coals was measured at 1250°C and residence time of 50 and 100 ms. The amount of N-species devolatilized as a fraction of the original coal nitrogen is listed in Table 2. HCN was the predominate species, however, a relatively large fraction of NOx was measured in these tests. It is improbable that NOx was a primary devolatilization product. HCN has been found to be the main product of pyrolysis of N-heterocyclic compounds and accounts for up to 95% of the primary gas phase N-products from coal [14, 15]. The high concentration of NOx and NH_3 measured in these experiments was probably due to secondary reactions of nitrogenated tars with the preheated gas [16, 17]. Few measurements were made in this investigation at residence time less than 50 ms, and no attempt was made to differentiate between primary devolatilization products and products of rapid secondary reactions.

Effect of Coal Type

In general, the bituminous coal type had a small effect on the NOx conversion in the reburning zone. The Scotts Branch and Obed Mountain coals had very similar behaviour in most experiments and the Hugo coal was approximately 10% less effective in reducing NOx (see Figure 3). The results indicated that there was little difference between the reburning performance of bituminous coals with different volatile matter contents.

Effect of Particle Size Distribution

The significance of PSD on reburning performance was very low. In comparative tests for Hugo and Obed Mountain coals, the difference in NOx concentration between micronized and normal grind coals was generally within experimental error. The insensitivity of reburning effectiveness to PSD implies that NOx reduction on the external surface of char particles was not of primary importance. In practice, particle size may be reduced to improve carbon burnout without altering the reburning performance.

Effect of Reburn Fuel Fraction and Primary Stoichiometry

The effect of reburn fuel fraction and primary stoichiometry are displayed in Figure 3. Each plot has a constant temperature of 1250°C, fine grind coal and inlet NOx of 400 ppm. Although each of the variables had separate effects, NOx reduction was more effectively described by the secondary stoichiometry which is a function of both the primary stoichiometry and the reburn fuel fraction. In Figure 3, the front, right-hand edge of each response surface represents a secondary stoichiometry of 0.7 and the back left-hand edge represents a secondary stoichiometry of 1.1. At 1250°C, the predicted NOx concentration decreased from 480 ppm to 140 - 210 ppm as the secondary stoichiometry decreased from 1.1 to 0.7. Secondary stoichiometry had a similar effect on NOx reduction at gas temperature of 1400°C as illustrated in Figure 4. At 0.3 s staging residence time and 400 ppm inlet NOx concentration, the measured NOx concentration decreased from 300 - 400 ppm to 30 - 100 ppm as secondary stoichiometry decreased from 1.0 to 0.73.

The maximum NOx reduction does not always coincide with the lowest TVFN concentration. The effect of reburn fuel fraction and primary stoichiometry on TVFN reduction is shown in Figure 5 for the same conditions used to create Figure 3. The surfaces in Figure 5 have a saddle shape with a peak in TVFN concentration at secondary stoichiometry of 0.7 and 1.1. The lowest concentration was predicted along a line where the secondary stoichiometry was between 0.86 and 0.96. The optimum secondary stoichiometry to minimize the TVFN concentration was coal dependent. The minimum TVFN concentration for Hugo coal was at a secondary stoichiometry of 0.86 compared to 0.96 for Obed Mountain coal. This was probably due to the higher fraction of devolatilized N-species from Obed coal (see Table 2).

Effect of Temperature

The reburn zone temperature had the greatest influence on the NOx reduction potential. The effect of temperature and secondary stoichiometry on NOx reduction, for Scotts Branch coal at an inlet NOx concentration of 400 ppm and residence time of 0.3 s, is illustrated in Figure 6. At a temperature of 1100°C, the secondary stoichiometry had little effect on NOx reduction and a concentration of 260 - 300 ppm was measured. At 1400°C, the secondary stoichiometry had a strong effect with NOx concentrations decreasing from 350 ppm to 50 ppm as the stoichiometry decreased from 1.0 to 0.8. The fact that a reburning zone temperature of 1400°C was necessary to obtain a NOx concentration of less than 100 ppm is in agreement with conclusions made in the literature [18, 19].

The decrease in TVFN concentration at higher temperature was due to the reduction of both NOx and HCN. The NH_3 concentration tended to rise at higher temperature due to NO and HCN destruction, however, with sufficient reburning residence time, the NH_3 would also be reduced. This is shown in Figure 7, which contains surface response curves for the NOx and TVFN concentrations as a function of temperature and time. The curves were generated for 20% reburning fuel using Scotts Branch coal at a primary stoichiometry of 1.0 (secondary stoichiometry equal to 0.8) and an inlet NOx concentration of 400 ppm. At 1100°C, the NOx and TVFN concentrations were insensitive to residence time; the outlet NOx and TVFN concentrations were approximately 280 and 500 ppm after 0.1 s with little reduction thereafter. This suggests that the initial staging reactions were completed in less than 0.1 s and additional residence time was not effective in reducing the NOx or TVFN concentrations. At 1400°C the NOx and TVFN continued to decrease at longer residence time. To achieve a NOx concentration of less than 100 ppm, residence time greater than 0.2 s was necessary at a temperature of 1400°C and secondary stoichiometry of 0.8.

Effect of Inlet NOx Concentration

The fractional conversion of NOx increased with higher inlet NOx, however, reduction was only possible under selected conditions at 200 ppm inlet NOx concentration. The effect of inlet NOx concentration on NOx reduction at different temperatures is illustrated in Figure 8. The data are presented for Scotts Branch coal at secondary stoichiometry of 0.8 - 0.9 and a residence time of 0.3 to 1.0 s. At 1100°C, the outlet NOx concentration increased from 220 to 400 ppm as the inlet NOx concentration increased from 250 to 600 ppm. At a temperature of 1400°C, the outlet NOx concentration was approximately 50 ppm and was independent of inlet NOx concentration. This indicated that the NOx may be almost completely reduced in 0.3 - 1.0 s for an inlet NOx concentration of up to 600 ppm.

For industrial application, this suggests that the reburning fuel should be injected into a region of the flame where NOx is concentrated. This would maximize the NH_3 concentration early in the reburning zone resulting in the rapid reduction of the remaining NOx. In a coal flame, large gradients in NOx concentration may exist prior to tertiary air injection [20]. If these gradients also exist across a furnace section, a detailed understanding of the NOx concentration profile could be used to determine the optimal reburning fuel injection location.

Effect of Residence Time

Residence time had a strong influence on NOx and TVFN reduction at all process conditions. A residence time greater than 0.3 s was necessary in order to obtain absolute NOx concentrations less than 100 ppm (see Figure 7). Three tests were selected for detailed measurement of N-species (DF1, DF2, DF3). These tests were the most effective process conditions for TVFN reduction.

The rate of NOx reduction from the detailed flames was predicted using a model for NOx decay in staged flames [21, 22]. The model makes no account for CH_i/NO type reactions but is based on the mechanism:

$$NH_i + NO \rightarrow N_2 + \text{products} \qquad (R2)$$
$$N + NO \rightarrow N_2 + O \qquad (R3)$$

The concentrations of NH_i species, where i may vary from 1 to 3 were assumed to be in semi-equilibrium according to the reaction:

$$NH_i + OH \Leftrightarrow NH_{i-1} + H_2O \qquad \text{(R4)}$$

The OH radical concentration was also assumed to be in equilibrium.

The equations which describe the rate of NO and HCN decay in the furnace are:

$$\frac{1}{[NO]} \frac{d[NO]}{dt} = - [NH_3] \times \phi_1(OH,T) \qquad (1)$$

$$\frac{1}{[HCN]} \frac{d[HCN]}{dt} = - [OH] \times \phi_3(T) - \frac{[OH]^2}{[H_2O]} \times \phi_4(T) \qquad (2)$$

where ϕ_1, ϕ_3 and ϕ_4 are functions of the OH radical concentration and temperature.

The change in N-species concentration was calculated using the measured HCN, NH_3 and NOx concentrations from the detailed flames. The calculations began at 0.05 s to separate the effects of devolatilization and the CH_i/NO reaction (Reaction 1) from Reactions 2 - 4. The H_2O concentration was calculated from the inlet CO_2 concentration and from the known ratio of CO_2/H_2O in the products of combustion for natural gas.

Detailed Flame 1. The first detailed flame was measured at a temperature of 12504°C and a secondary stoichiometry of 0.75. The inlet NOx concentration was set to 400 ppm and the O_2 concentration to 0%.

The measured concentrations of nitrogen species and permanent gases are shown in Figure 9. The NOx concentration decreased from 330 ppm at 0.05 s to 180 ppm at 1.0 s. The concentrations of HCN and NH_3 rapidly increased in the first 0.1 s. The rapid increase could be partially attributed to the devolatilization of nitrogen species from the reburning fuel. Approximately 150 of the 200 ppm of HCN and 60 of the 90 ppm of NH_3 would be expected to come from the coal devolatilization based on separate measurements (see Table 2). The remainder was probably attributed to fuel staging reactions. After 0.1 s, the HCN decayed from 200 to 90 ppm and the NH_3 increased from 90 to 165 ppm. The NH_3 was formed from the conversion of HCN. Once NH_3 was formed, there was a very slow conversion to N_2. Therefore, at 1250°C, residence time greater than 1.0 s would be required to further reduce TVFN using reburning. This may not be acceptable in industrial application.

The rate of NOx and HCN reduction in DF1 was underpredicted using the NOx decay model. It may be possible that the OH radical concentration was not in equilibrium at these conditions. Bose et al [21] noted that the OH radical concentration was greater than equilibrium in rapidly cooled flames. Using the OH radical concentration, suggested by Bose et al, led to overprediction of the rate of NOx and HCN reduction [23].

Detailed Flame 2. The second detailed flame was measured at a reaction temperature of 1400°C, primary stoichiometry of 1.0 and NOx concentration of 400 ppm. Secondary stoichiometry was set to 0.75 by injecting 25% reburning fuel fraction. It was foreseen that this condition may be applicable to industrial and utility boilers.

The concentration of nitrogen species and permanent gases as a function of residence time is shown in Figure 10. The NOx concentration decreased from 400 to 30 ppm as the residence time increased from 0 to 1.0 s. It was estimated, from separate experiments, that the TVFN concentration from devolatilization was 340 ppm. The TVFN concentration was reduced to 490 ppm in 0.05 s and from 490 to 330 ppm up to 1.0 s. Rates of TVFN and the NOx reduction in the first 0.05 s were an order of magnitude faster than after 0.05 s indicating that a different mechanism was predominant during initial reduction. The HCN concentration increased in the first 0.05 s to 150 ppm and decreased to 25 ppm thereafter. Although 150 ppm HCN was equal to the devolatilization yield from the coal, there was undoubtedly HCN formed from the CH_i/NO reaction (Reaction 1). The reduction of NOx to HCN was probably occurring at a similar rate as the reduction of HCN to NCO. The NH_3 yield continued to increased to a final value of 290 ppm. After 0.3 s, NH_3 was the only significant nitrogen species.

The model accurately predicted the NOx and HCN concentrations up to the furnace position where their concentrations equalled 25 ppm. After this point, the model predicted that the NOx and HCN concentrations tended to zero whereas a residual concentration of 10-25 ppm was measured in the reactor. This suggests that the OH radical concentration was in equilibrium at these conditions.

The results for DF2 suggest that this process configuration would be suitable for application in a utility boiler. The reduction of NOx was rapid and complete in 0.3 s, although it would be necessary to reduce a fraction of the NH_3 to N_2 in the tertiary combustion zone to minimize NOx reformation.

Detailed Flame 3. The third detailed flame was measured at a temperature of 1400°C, inlet stoichiometry of 1.075 and 400 ppm NOx. The secondary stoichiometry was set to 0.85 by injecting 25% reburning fuel.

The concentrations of N-species and permanent gases are illustrated in Figure 11. The NOx concentration decreased from 400 ppm to 20 ppm over 1.0 s. The rate of reduction of NOx was slower than for DF1 or DF2. This was expected because the HCN and NH_3 concentrations were only 19 and 15 ppm after 0.05 s resulting in a slower rate of NO destruction. The HCN and NH_3 concentrations were much lower than measured under devolatilization conditions suggesting that they were rapidly converted in the reactor. No oxygen was measured in the reactor at 0.05 s, indicating that the process was rapid and complete. The NOx gradually decreased to 20 ppm with only a small increase in the concentration of NH_3. This resulted in a lower TVFN after 1.0 s (130 ppm) than was achieved in DF1 or DF2.

The model accurately predicted the NOx concentrations in DF3. The rate of NOx reduction was slower than in DF2 since the concentration of NH_3 was an order of magnitude less. There was sufficient NH_3 to cause complete reduction of NOx in 1 s.

The success of this relatively simple model to predict NOx and HCN reduction is useful in understanding reburning. It implies that the rate of NOx reduction may be modelled with a knowledge of the NH_3 concentration and the reactor temperature. Therefore, the CH_i/NO reaction (Reaction 1) which dominated the reduction in the first 0.05 s may be separated from the nitrogen reduction reactions which dominated after 0.05 s. The reduction scheme reported is applicable to both air and fuel staging processes, and therefore, may be incorporated into a relatively simple NOx reduction model for both systems.

It may be postulated that a sufficient NH_3 concentration was necessary to reduce NOx in the reactor after 0.05 s. In coal fuel staging, this NH_3 may be formed from the coal volatile nitrogen products or from the reburning process itself. If the

NOx and NH_3 concentrations are equal after 0.05 s, Reaction 2 would proceed rapidly and the NOx and NH_3 could be completely converted to N_2. In practice, balancing the NOx and NH_3 concentrations may be difficult to achieve. However, this concept suggests guidelines for the implementation of fuel staging in furnaces.

CONCLUSIONS

The following conclusions may be made regarding the importance of the measured process variables on fuel staging.

Bituminous coal type had a small effect on NOx reduction. High volatile bituminous coals could reduce NOx over a wider range of operating conditions. Medium volatile bituminous coal could be used to reduce NOx.

Particle size distribution was not a significant parameter affecting NOx or TVFN reduction. This indicates that particle size may be varied without altering fuel staging performance.

The effects of reburning fuel fraction and primary stoichiometry on NOx reduction were strong. These two variables could be transformed to a single variable, the secondary stoichiometry. The concentration of NOx decreased with secondary stoichiometry, however, TVFN was minimum at a secondary stoichiometry of 0.8 - 0.9. Coals with a larger fraction of volatile matter required a higher secondary stoichiometry to minimize TVFN concentration.

Temperature had a strong effect on NOx and TVFN reduction. At 1100°C, the NOx concentration was reduced from 400 ppm to a minimum of 260 ppm. At 1400°C, the NOx concentration was reduced from 400 ppm to 30 ppm. Higher temperature promoted rapid decay of HCN and NH_3 to N_2.

The fractional conversion of NOx usually increased as inlet NOx concentration increased. At 1400°C, the outlet NOx concentration was independent of the inlet NOx concentration and NOx was reduced from 200 - 600 ppm to 50 ppm in 0.3 - 1.0 s. The inlet NOx concentration had little effect on the concentrations of HCN or NH_3. It was concluded that the NOx and NH_3 could rapidly react together to form N_2 at the conditions studied.

Residence time greater than 0.3 s was necessary to obtain NOx concentrations less than 100 ppm. The time to reduce NOx was dependent on the temperature and the secondary stoichiometry. Less time was required to reduce the NOx at a higher temperature and lower secondary stoichiometry.

The NOx and HCN reduction occurring after 0.05 s could be accurately predicted by a simple model for NOx reduction in air staged flames. This suggested that the CH_i/NO reaction was complete before 0.05 s and the NH_i/NO reaction dominated thereafter.

Application of fuel staging in burners or furnaces may be limited by the residence time at high temperature necessary for complete NOx and TVFN reduction. Assuming good mixing, a residence time of 1.0 s at 1400°C should be sufficient to completely reduce NOx to less than 50 ppm and TVFN to less than 150 ppm. Lower temperature and shorter residence times result in higher concentrations of both NOx and TVFN.

ACKNOWLEDGEMENTS

The IFRF would like to acknowledge that the work described in this report was executed on behalf of and supported financially by organisations in Canada, the

Federal Republic of Germany and the Netherlands. The programme has been organised under the auspices of the International Energy Agency and forms part of Annex II of the implementing agreement for a programme of research, development and demonstration of coal combustion sciences.

REFERENCES

1. Y. Takahashi et al. "Development of Mitsubishi "MACT" In-furnace NOx removal process". Presented at US-Japan NOx Information Exchange, Tokyo, May 25 - 30, 1981.

2. R. Waibel and D. Nickeson. "Staged fuel burners for NOx control". Presented at IFRF 8th Members Conference, Noordwijkerhout, the Netherlands, May 28 - 30, 1986.

3. J. A. Mulholland and R. E. Hall. "Fuel oil reburning application for NOx control to firetube package boilers". Presented at the Joint ASME/IEEE Power Generation Conference, Milwaukee, October 20 - 24, 1985.

4. W. S. Lanier, J. A. Mulholland and J. T. Beard. "Reburning thermal and chemical processes in a two-dimensional pilot scale system". Twenty-first Symposium (International) on Combustion, The Combustion Institute, Pittsburgh, 1988 (in press).

5. Y. H. Song, D. W. Blair, V. J. Siminski and W. Bartok. "Conversion of fixed nitrogen to N_2 in rich combustion". Eighteenth Symposium (International) on Combustion, The Combustion Institute, Pittsburgh, 1981, pp 53 - 63.

6. Y. H. Song and W. Bartok. "Rate controlling reactions in fixed nitrogen conversion to N_2". Nineteenth Symposium (International) on Combustion, The Combustion Institute, 1982, pp 1291 - 1299.

7. S. L. Chen, J. M. McCarthny, W. D. Clark, M. P. Heap, W. R. Seeker and P. W. Pershing. "Bench and pilot scale process evaluation of reburning for in-furnace NOx reduction". Twenty-first Symposium (International) on Combustion, The Combustion Institute, Pittsburgh, 1986.

8. J. A. Mulholland and R. E. Hall. "The effect of fuel nitrogen in reburning application to a fire tube package boiler:. Proc of 1985 Joint Symp on stationary combustion NOx control, Vol 1, No. 4, 1986.

9. W. J. Phelan. The effect of pulverised coal type and burner parameters when staging air combustion for NOx reduction, International Flame Research Foundation, IFRF Doc.No. K 20/a/180.

10. R. J. Roby and C. T. Bouwman. "Effects of hydrocarbons on nitric oxide removal in rich premixed hydrogen oxygen flames". Presented at The Combustion Institute, Canadian and Western States, Spring 1986 section meeting, Banff, Canada, April 27 - 30, 1986.

11. J. O. L. Wendt, C.V. Sternling and M. A. Matovich. "Reduction of sulphur trioxide and nitrogen oxides by secondary fuel injection". Presented at Fourteenth Symposium (International) on Combustion, The Combustion Institute, Pittsburgh, 1973, pp 897 - 904.

12. J. P. Smart and T. Maalman. An analytical procedure for the quantitative determination of NH_3 and HCN in combustion systems, International Flame Research Foundation, IFRF Doc.No. F 72/a/10, October 1987.

13. G. E. P. Box and P. W. Behnkin. "Some new three level designs for the study of quantitative variables". Technometrics, Vol 2, 1960.pp 455 - 475.

14. J. D. Freihaut, W. M. Proscia and D. J. Seery. "Fuel bound nitrogen evolution during the devolatilization and pyrolysis of coals of varying rank". Presented at 1987 Joint Symposium on stationary combustion NOx control, New Orleans, March 23 - 26, 1987.

15. J. D. Freihaut and D. J. Seery. "Evolution of fuel bound nitrogen during the vacuum thermal devolatilization of coal". ACS Preprints, Volume 26 No. 3, New York, August 23 - 28, 1981.

16. R. E. Peck, R.A. Altenkirch and K. C. Midkiff. "Fuel nitrogen transformations in one-dimensional coal-dust flames". Combustion and flame, Volume 55, 1984, pp 331 - 340.

17. S. L. Chen, M. P. Heap, D. W. Pershing and G. B. Martin. "Influence of coal composition on the fate of volatile and char nitrogen during combustion". Nineteenth Symposium (International) on Combustion, The Combustion Institute, 1982, pp 1271 - 1280.

18. L. R. Thorne, M. C. Branch, D. W. Chandler, R. J. Kee and J. A. Miller. "Hydrocarbon/nitric oxide interactions in low pressure flames". Presented at 1986 spring meeting of the Canadian and Western States sections of the Combustion Institute, Banff, April 28 - 30, 1986.

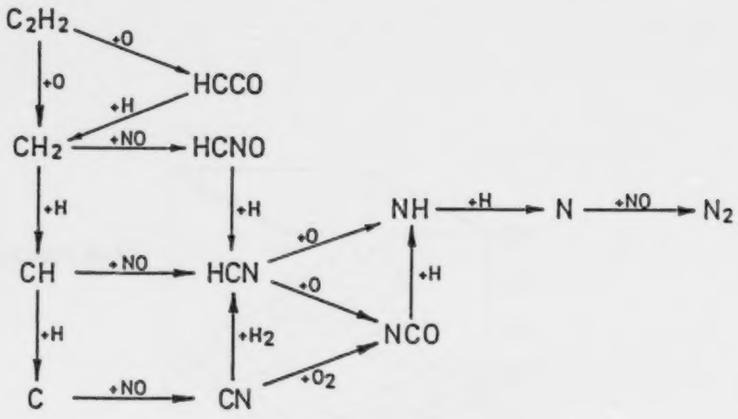
19. W. F. Farnmayan, M. Togan, Yu. Tae-u, J. D. Tear and J. M. Beer. "Reduction of NOx emission from natural gas flames by staged fuel injection". Proc 1985 Joint Symp on stationary combustion NOx control, Boston, May 6-9, 1985.

20. R. Weber, J. P. Smart and W. J. Phelan. NOx reduction with coal firing by application of both internal air staging and fuel rich precombustors, International Flame Research Foundation, IFRF Doc.No. F 037/a/16, February 1987.

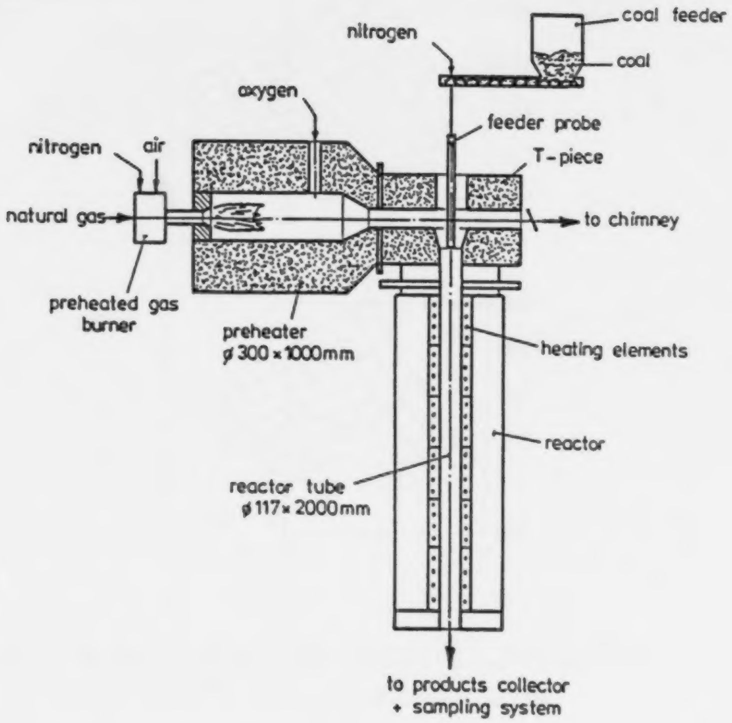
21. A. C. Bose and J. O. L. Wendt. "Pulverized coal combustion: Fuel nitrogen mechanisms in the rich post-flame region". Twenty-second Symposium (International) on Combustion, the Combustion Institute.

22. A. C. Bose, K. M. Dannecker and J. O. L. Wendt. "Coal composition effects on mechanisms governing the destruction of NO and other nitrogeneous species during fuel rich combustion". Journal of Energy and Fuels.

23. K. K. Knill, J. S. A. Dekker and M. E. Morgan. Evaluation of the Effect of Process Variables on NOx and Nitrogen Species Reduction in Coal Fuel Staging. International Flame Research Foundation, IFRF Doc.No. F 037/a/20, November 1988.



Fig·1: Model for NOx reduction by fuel staging



Fig·2: Schematic of the isothermal plug flow reactor

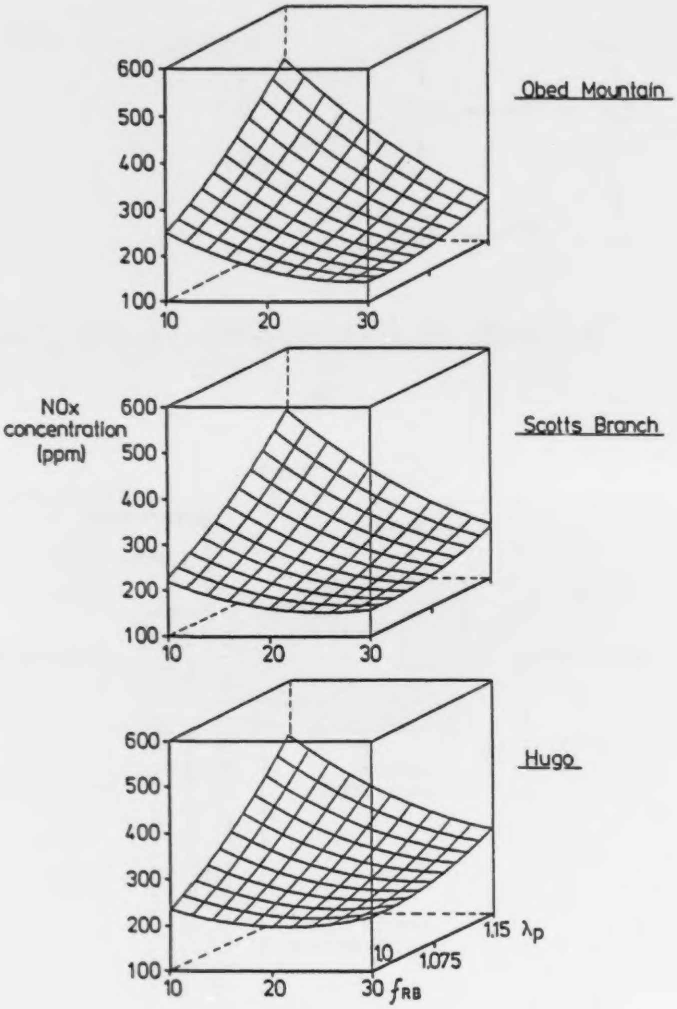


Fig.3:Effect of reburn fuel fraction and primary stoichiometry on NOx concentration

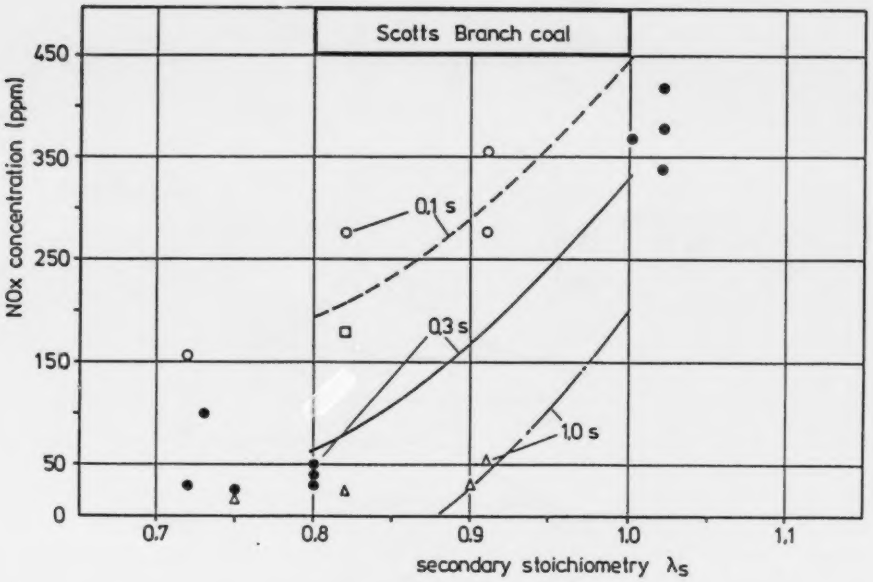


Fig.4: Effect of secondary stoichiometry and residence time on NOx concentration

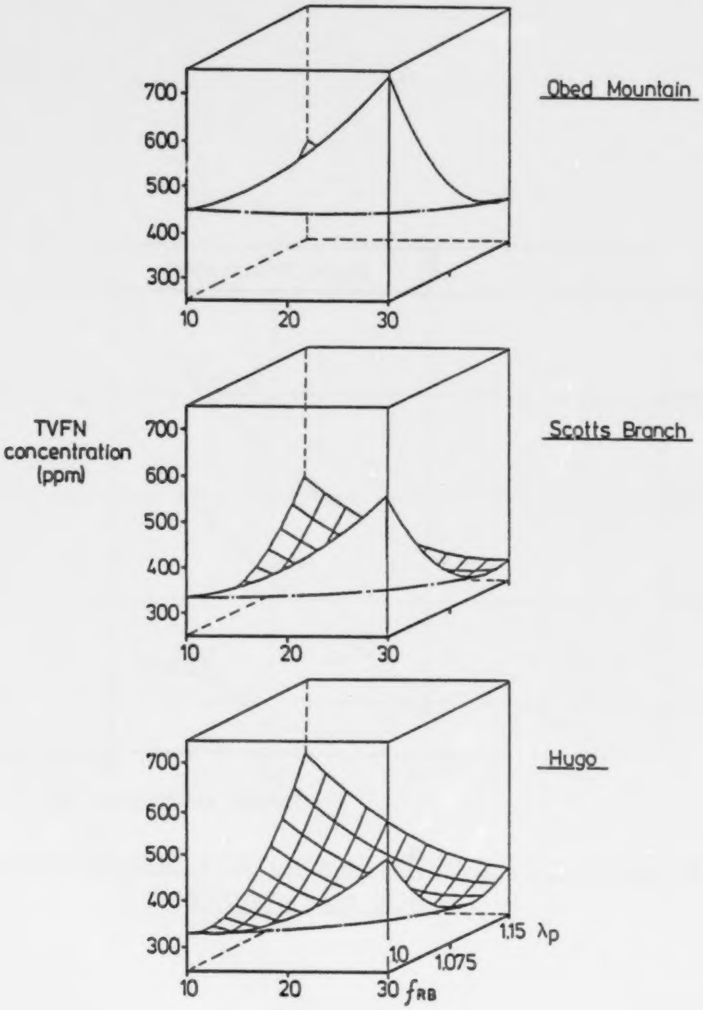


Fig. 5: Effect of reburn fuel fraction and primary stoichiometry on TVFN concentration

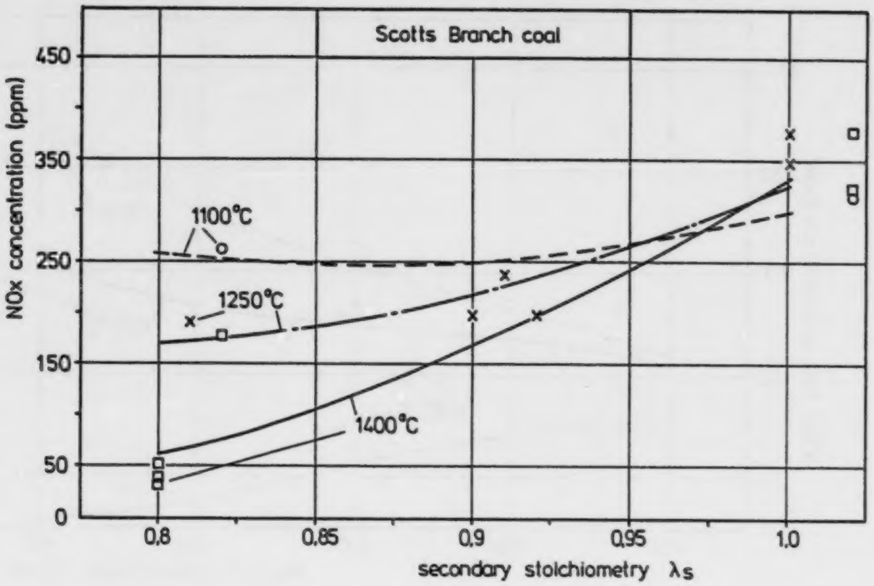


Fig. 6 : Effect of secondary stoichiometry and temperature on NOx concentration

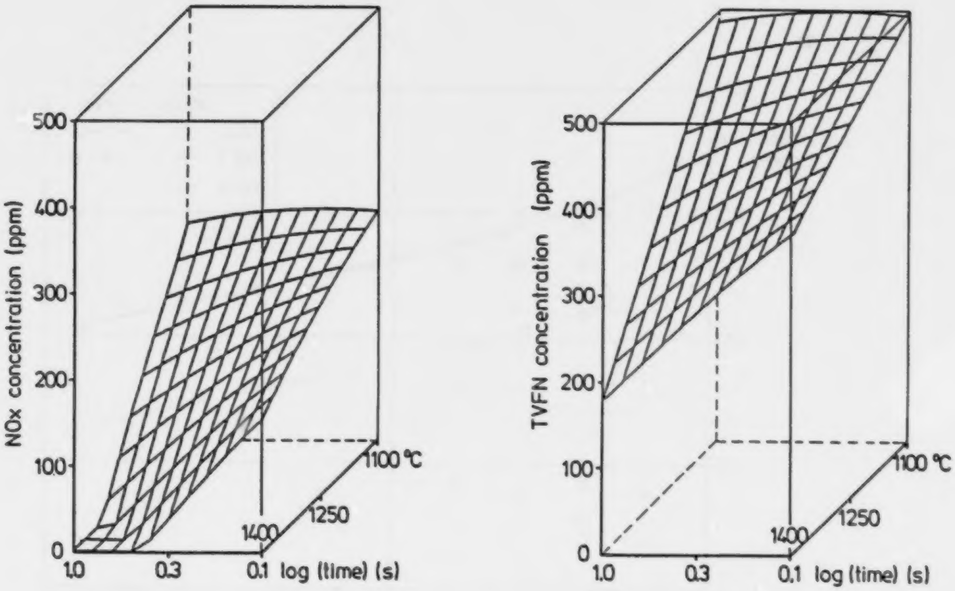


Fig. 7 : Effect of temperature and residence time on NOx and TVFN concentrations

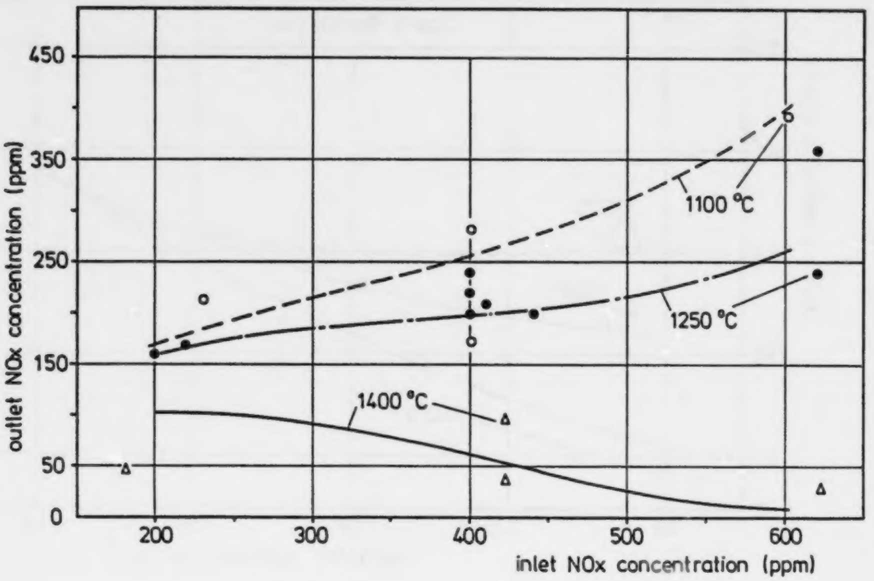


Fig. 8 : Effect of inlet NOx concentration on outlet NOx concentration at different temperatures

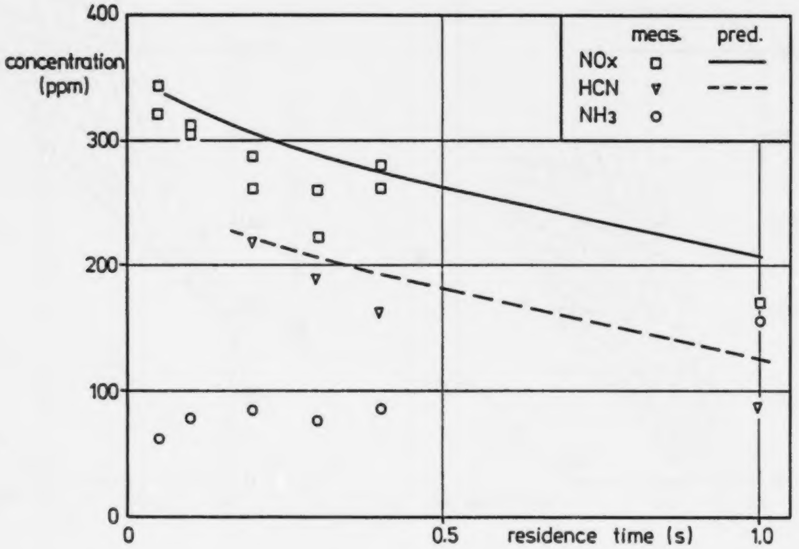


Fig. 9 : N-species profiles for detailed flame 1

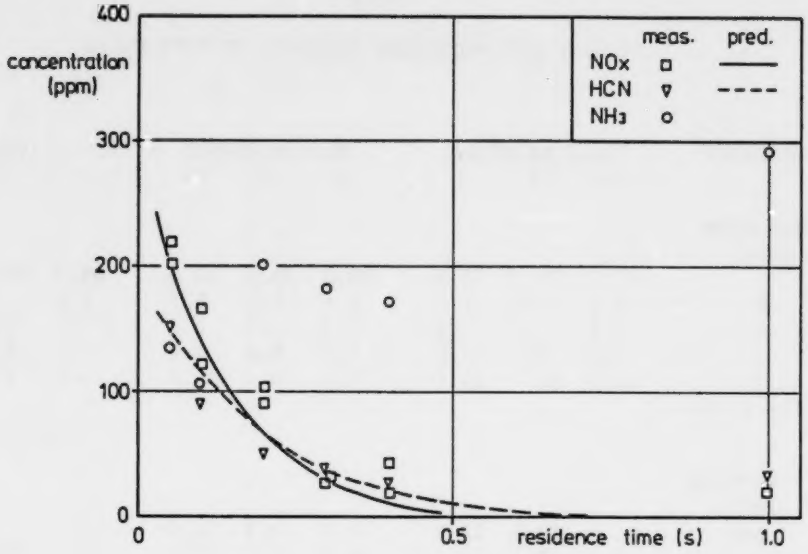


Fig.10: N-species profiles for detailed flame 2

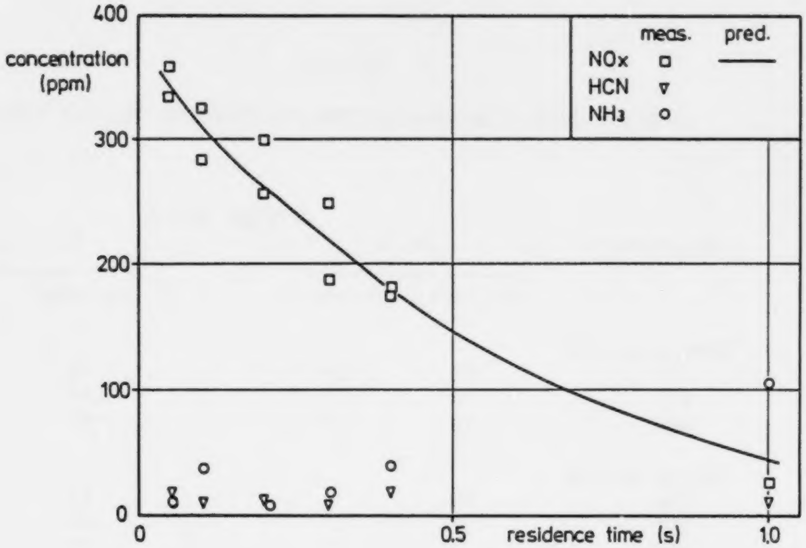


Fig.11: N-species profiles for detailed flame 3

Table 1

ULTIMATE AND PROXIMATE ANALYSES OF TEST COALS

ANALYSIS	Obed Mountain			Scotts Branch			Hugo		
	m	f	n	m	f	n	m	f	n
ULTIMATE (DAF)									
C	72.7	72.8	72.5	82.2	82.2	82.2	88.3	88.1	88.1
H	4.6	4.6	4.7	5.1	5.2	5.1	4.8	4.8	4.8
N	1.8	1.8	1.8	1.7	1.7	1.7	1.7	1.7	1.7
S	0.6	0.5	0.6	0.5	0.5	0.5	0.7	0.7	0.7
O (by diff)	20.3	20.3	20.4	10.5	10.4	10.5	4.5	4.7	4.7
PROXIMATE (DRY)									
Ash	14.2	14.2	14.2	8.1	8.1	8.0	7.1	7.1	7.1
- Volatile matter	36.3	36.3	36.2	34.2	34.5	34.6	22.9	23.0	23.1
- Fixed carbon	49.5	49.5	49.6	57.7	57.4	57.4	70.0	69.9	69.8

m = micronized grind; f = fine; n = normal

Table 2

DEVOLATILIZED NITROGEN SPECIES MEASURED IN THE GAS PHASE.

COAL/SPECIES	SPECIES YIELD			
	0.05 s		0.10 s	
	Vol(ppm)	wt%-N	vol(ppm)	wt%N
Obed Mountain				
NH_3	102	19	99	19
HCN	150	27	144	26
NOx	50	9	40	7
Scotts Branch				
NH_3	40	8	63	12
HCN	132	25	151	29
NOx	120	23	120	23
Hugo				
NH_3	48	8	40	7
HCN	48	10	40	11
NOx	35	7	35	7

NO_x EMISSIONS IN A PILOT SCALE CIRCULATING FLUIDIZED BED COMBUSTOR

J. Zhao, J.R. Grace, C.J. Lim, C. Brereton and R. Legros
Department of Chemical Engineering
University of British Columbia
2216 Main Mall
Vancouver, Canada V6T 1W5
and E.J. Anthony
CANMET, Energy, Mines and Resources
555 Booth Street
Ottawa, Canada K1A 0G1

ABSTRACT

A variety of fuels, including woodwastes, several coals and pitch, have been burned in a pilot scale circulating fluidized bed combustor of cross-section 0.15 m by 0.15 m and height 7.3 m. NO_x emissions were in the range 80-220 ppm (40-110 mg/MJ), depending on the fuel type, and operating conditions. These emissions increased with bed temperature, excess air ratio and the feed rate of limestone used for in situ capture of sulphur. For coals with similar nitrogen contents, NO_x emission levels are higher for coals having higher volatile contents. Preliminary measurements of radial NO_x concentration profiles indicate that there are substantial gradients between the wall region and the centre of the combustor. This phenomenon must be understood if results are to be scaled to large units.

INTRODUCTION

As an outgrowth of conventional fluidized bed (bubbling bed) combustion, circulating fluidized bed combustion (CFBC) has found increasing applications in the combustion of a wide variety of fuels, such as coal, peat, woodwaste and oil (1). Circulating fluidized beds operate in the fast fluidization regime as a relatively concentrated suspension of mean density typically 15-80 kg/m^3 with a superficial gas velocity of the order of 5-12 m/s. Solid particles (with a mean diameter of 50-500 microns) are carried over from the top of a riser, captured by cyclones or other gas/solid separators and returned to the base of the riser through non-mechanical valves (e.g. L-valve) or seals.

The major advantages of CFBC compared with conventional fluidized beds are fuel flexibility, improved turndown, higher combustion efficiency and lower pollutant emissions (2). Favourable NO_x emissions (typically 100-200 ppm) have been reported (e.g. 3).

In spite of the increasing interest in CFB combustion, little information has been reported concerning NO_x emissions and the factors which control these emissions under the conditions of CFBC. By contrast, NO_x formation and reduction mechanisms in conventional fluidized bed combustion (FBC) have been investigated fairly thoroughly.

It is generally accepted that formation of NO_x in bubbling fluidized bed combustors is predominantly by oxidation of fuel-bound nitrogen. Temperature has a strong effect on NO_x emission. In one study Gibbs et al. (4) reported that in the range 650-850°C, NO_x increases linearly with temperature at a rate of 2.6 ppm/°C. Thermal NO (i.e. NO derived by oxidation of nitrogen in the air) is not detectable for temperatures of 800°C or below (5).

Excess air ratio is another major factor affecting NO_x formation. It is clear that NO_x emissions increase with the excess air ratio. For example, Hirama et al. (6) found that NO_x emissions almost doubled when the excess air ratio was increased from 1.0 to 1.25. Bed materials may have a catalytic effect on NO formation. According to Hirama et al., among the bed materials tested (silica sand, coal ash and limestone), limestone gave the highest NO_x. Clearly the composition of the particular limestone may also play a role.

Detailed study of NO formation and reduction in bubbling fluidized bed combustion of coal was conducted by Beer and colleagues (7). Axial profiles of NO concentration were measured in an experimental unit. It was found that NO is produced in the bubbling bed, then substantially reduced in the freeboard due to the reduction of NO by char.

Staged combustion has been stated to be an effective way to reduce NO_x emission from fluidized bed combustion. However, Hirama et al. (8) reported that staged combustion had little effect on NO_x emission in CFB combustion, unless fresh limestone is used.

Although CFBC and bubbling FBC have many similarities, the mechanism of NO_x emission may differ in important respects. The objective of this paper is to show the experimental effects of operating variables on NO_x emissions based on a well-instrumented pilot plant CFBC unit. Axial and radial concentration profiles are presented in order to provide an improved understanding of the mechanisms and factors affecting NO_x emissions.

EQUIPMENT AND INSTRUMENTATION

UBC CFBC Facility

A schematic of the UBC CFBC facility appears in Fig. 1. The combustor is a 7.3 m tall by 0.15 m square refractory-lined column. Air is fed into the combustor through a primary air distributor at the base. Secondary air is introduced 0.9 m above the base either as opposed jets or with swirl. The ratio of secondary to primary air can be varied over a wide range. During start-up, the primary air is preheated by natural gas through a gas burner. The secondary air can be preheated during operation by the flue gas. A variety of fuels can be fed by a screw feeder, by a rotary valve or by a gear pump (for liquid fuels only). Heat can be removed from the riser by an instrumented membrane wall cooling surface or by vertical internal stainless steel tubes. Entrained solids leaving the top of the riser are separated by a refractory-lined primary cyclone and fall through a storage hopper into a standpipe. Solids are then returned to the bottom of the riser by an L-valve, at rates which are controlled by air injection. Gas containing entrained fine particles leaving the primary cyclone passes through a secondary cyclone, a jacketed cooling section and a baghouse. Fine solids captured by the secondary cyclone are recycled back to the bottom of the riser via an eductor. The combustor assembly is provided with a series of thermocouples, pressure taps, sight glass and sampling ports. More detailed descriptions of the UBC CFBC pilot plant are provided elsewhere (9,10).

Instrumentation and Gas Sampling System

During the experiments, temperatures, pressures and flue gas compositions are recorded by a computer at five-minute intervals. Flue gas is monitored continuously by a series of on-line gas analyzers, including non-dispersive infrared (NDIR) analyzers for sulphur dioxide, hydrocarbon, carbon monoxide and carbon dioxide, a chemiluminescent analyzer for nitric oxides (NO and NO_2), and a paramagnetic analyzer for oxygen. Gas samples can also be withdrawn from a sampling port between the primary and secondary cyclones. The combustor is operated at small pressures, forcing the sample gas to pass through a stainless steel filter, a cooling coil, a water trap (ice bath) and a drying tube to remove moisture before reaching the gas analyzers.

In order to understand the mechanism of pollutant formation and provide useful data for mathematical modelling, a multiposition sampling system was installed. As shown in Fig. 2, sample gas can be withdrawn at five different heights along the combustor. After passing through a filter, sample gas is cooled by a water-cooled heat exchanger. Condensed water is drained from the bottom of the exchanger. A drying tube filled with magnesium perchlorate ($Mg(ClO_4)_2$) is used to remove further moisture before the sample gas reaches the manifold on the control panel. Air purges can be used to flush out solids from the filters when samples are not being taken. The gas probe, made of stainless steel, is connected to the filter by flexible stainless steel tubing allowing the gas sampling probes to be moved to different radial positions. The five sampling levels are shown in Fig. 2.

EXPERIMENTAL RESULTS AND DISCUSSION

Operating Conditions

For most of the combustion tests, bed temperatures were in the range 850-900°C. Typical steady-state temperature distributions are given in Fig. 3 for several fuels. Superficial gas velocities above the secondary air injection ports are 6-10 m/s. The secondary-to-primary air ratio is usually maintained in the range 0.5-2.0. The excess air ratio is 1.17-1.24, giving 3-4% oxygen in the flue gas. Approximately 100 kg of olivine sand (density 3066 kg/m^3) with a mean diameter of about 240 microns is used for start-up.

NO_x Emission from Combustion of Different Fuels

In early combustion tests, three different coals (Esso, Highvale and Minto), two pitches and two woodwastes (sawdust and hogfuel) were burned. These runs were performed without ash recycle from the secondary cyclone. The operating conditions and NO_x emissions for some runs are given in Table 1, while fuel analyses are provided in Table 2.

As indicated in Table 1, higher NO_x emissions occur when there is a higher nitrogen content of the fuel. The net molar conversion of fuel nitrogen to NO_x (moles NO_x emitted/moles N in the fuel fed) were 0.17, 0.59 and 0.16 for Minto coal, hogfuel and CANMET pitch, respectively. The ratios are in the range 0.05-0.2, suggested by Becker et al. (11) for coal and pitch. However, it seems that the combustion characteristics of hogfuel are quite different as far as NO_x emissions are concerned, giving much higher emissions when expressed on this basis. This may be related to the high volatile content and low residence time of the woodwastes.

In order to increase the operational flexibility and to improve the sulphur capture and combustion efficiency of the CFB combustor, a series of modifications were made in early 1988 (10). The key changes which might have an effect on NO_x emissions were the provision for recirculation of the fines captured in the secondary cyclone, replacement of the bottom section of the riser by a diverging section, and a switch from screw feeding to pneumatic feeding of both solid fuel and sorbent. Since these modifications, four different coals, a Saskatchewan lignite, an Alberta low sulphur sub-bituminous coal (Highvale), a New Brunswick high sulphur bituminous coal (Minto) and a B.C. anthracite were burned. High combustion efficiency and sulphur capture were achieved in these runs (10,12). Analyses of these coals are also provided in Table 2. Some preliminary NO_x emission results follow.

Effect of Excess Air Ratio

Figure 4 shows the relationship between NO_x emission and excess air ratio for Highvale coal. The apparent linear increase of NO_x level with excess air shows the importance of controlling excess air in order to reduce NO_x emission. Twenty percent or less excess air (oxygen in flue gas < 3.5%) allowed the NO_x level to be maintained below 170 ppm for the conditions specified in Fig. 4.

Effect of Temperature

Although the effect of temperature on NO_x emission was found to be less strong than in bubbling bed combusion (e.g. (4)), increasing temperature does lead to higher NO_x emissions. For Highvale coal at 760 and 890°C, NO_x levels were 70 and 160 ppm for the same excess air. The rate of increase is about 0.8 ppm/°C.

Figure 5 shows the variation of temperature and NO_x after a step decrease in the fuel feed rate was made during a combustion test with the lignite. The temperature of the combustor gradually decreased from 850 to 725°C over a period of two hours while other conditions remained unchanged. NO_x in the flue gas decreased from 190 to 105 ppm. Note that the increase of CO level and carbon loading due to the lowered temperature may have also contributed to the reduction in NO_x emissions which occurred after the step decrease in the fuel feed rate.

Effect of Staged Combustion

There was no clear correlation between NO_x emission and secondary to primary air ratio for the conditions studied. Table 3 gives the NO_x emission for combustion of the B.C. anthracite. The slight change of NO_x emission when the secondary-to-primary air ratio was doubled shows that the effect of staged combustion for this particular combustor is small. Similar conclusions can be drawn also for other fuels, as seen in Table 1. In the current tests, secondary air was added only 0.9 m above the primary air, and it may be necessary for the secondary air entry to be much higher to have a noticeable beneficial staging effect. As pointed out by Hirama et al. (8), staged combustion in CFBC should be less effective than in conventional bubbling fluidized bed combustion.

Effect of Ca/S Ratio

Similar to the findings from some bubbling FBC units, e.g. (6), the influence of limestone on NO_x emission was quite strong. Typical results appear in Table 4. No_x emissions almost doubled when the molar Ca:S ratio increased from 0 to 3.0 for the conditions described.

Fuel Character and NO_x Emissions

From our experience with different fuels it would appear that both carbon content and the percentage volatile matter in the fuel may influence NO_x emissions. For example, under similar combustion conditions, the unreactive anthracite (Table 2), has a nitrogen content of 0.86%. Its NO_x emission is only about 90 ppm compared to 160 ppm from Highvale coal which has less nitrogen (0.71%). The low NO_x emission for the anthracite is probably related to its low volatile content (6.5%, compared to 31% for Highvale). A simple correlation which works well for the various fuels investigated in this work and for the data of Hirama et al. (8), all in the absence of limestone, is:

$$NO_x \text{ (ppm)} = 50\ V_N^{0.3} \tag{1}$$

where V_N is the product of the volatile matter from the proximate analysis and the nitrogen content from ultimate analysis of same fuel (N% x Volatile%). This correlation is only applicable for the conditions used in the two combustors which produced the data, i.e. for temperature 850-900°C, gas velocity 6-10 m/s, secondary to primary ratio 0-2.0, 15-30% excess air, abrupt exit geometry and no addition of limestone. As shown in Fig. 6, Eqn (1) gives a good fit for the wide range of nitrogen content (0.10-0.95%) and volatile matter (6-61%) covered by the fuels tested.

NO_x Concentration Profiles

To assist in the understanding of the mechanisms of NO_x formation and destruction, gas samples were withdrawn at different levels of the riser. With the system held at steady conditions, samples from different heights and different radial positions could then be analyzed, one after another.

Preliminary results (see Fig. 7) show that the basic pattern of axial profiles with samples taken at the wall is similar to those in bubbling beds, e.g. (7). At the bottom of the riser (below the coal feed port), the NO_x concentration is very low. However, a fast build-up of NO_x was found above the secondary air entry. A maximum concentration occurred between 15 and 30% of the way up the column, with the exact position depending on the operating conditions. NO_x levels then decrease continuously throughout the upper part of the riser. This pattern can be explained by the release of fuel nitrogen and subsequent reactions which may either enhance or abate the NO_x level. At the bottom, a turbulent dense bed exists. Fuels fed into the riser need time to devolatilize. Because of high gas velocity, typically 4-5 m/s below and 8-10 m/s above the secondary air injection port, the volatiles are released at greater heights. Also, due to the reducing conditions at the bottom of the riser, there is limited oxygen for NO_x to form. The catalytic effect of limestone under reducing conditions tends to suppress NO_x formation (13). Above the secondary air entry, the local oxygen concentration can be as high as 15%, and oxidation of fuel N can be catalyzed by the presence of limestone. After a maximum NO_x concentration is reached, reduction of NO_x by char causes the NO_x concentration to decrease substantially in the wall region, as shown in Fig. 7. Increasing the secondary-to-primary air ratio gives a higher NO_x concentration above the secondary air entry. However, NO_x levels converge and are essentially identical by the top of the column.

Because of different hydrodynamics between bubbling and circulating fluidized beds, the spatial concentration distribution of gas components may be very different. The annulus-core flow pattern in circulating fluidized beds may be expected to cause radial gradients. Preliminary results from a recent combustion test of Minto coal, in which NO_x concentrations at three radial positions were measured, are shown in Fig. 8. The three radial position are the axis of the riser, half-way between the axis and the wall and right at the wall itself. Similar to the earlier findings shown in Fig. 7, the concentration of NO_x dropped rapidly in the upper part of the reactor for samples taken at the wall. However, the concentration of NO_x was found to be almost uniform in the centre of the column. It is clear that local suspension density (which determines carbon loading) affects strongly the profiles of NO_x, as well as of other gaseous components. With high suspension density near the wall, more carbon can react with NO_x and there is less oxygen present. On the other hand, in the dilute core of the riser, the reduction of NO_x was less effective. It is clear that the suspension density distribution has a direct influence on NO_x formation and reduction in circulating fluidized bed combustion. More comprehensive analysis of these results is under way.

CONCLUSIONS

A variety of fuels, including woodwastes, coals and pitches, have been burned in a pilot scale circulating fluidized bed combustor. NO_x emissions were in the range 80-220 ppm. Among the operating variables, temperature, excess air ratio and limestone feed rate were found to have strong effects on NO_x emissions. No clear influence of the secondary-to-primary air ratio was found for the conditions investigated. NO_x emissions can be estimated from a simple correlation in which both fuel nitrogen content and volatile matter are used.

NO_x concentration profiles at different heights and radial positions were measured. Closely related to local suspension densities and oxygen concentrations, greater reduction of NO_x was found near the wall, where solid concentration and carbon loading were higher than in the dilute core of the reactor. It is clear that these radial differences need to be accounted for in modelling of nitrogen reactions in circulating fluidized bed combustors.

ACKNOWLEDGEMENT

The authors are grateful to Energy, Mines and Resources, Canada which provided the funds for this study. Assistance during the experiments from H. Ackroyd, H. Li, R. Senior and R. Wu is gratefully acknowledged.

REFERENCES

1. A. Kullendorff and S. Andersson. A General Review on Combustion in Circulating Fluidized Beds, in Circulating Fluidized Bed Technology, ed. P. Basu, Pergamon, Toronto, 83-96 (1986).

2. H. Kobro and C. Brereton. Control and Fuel Flexibility of Circulating Fluidized Beds, in Ciculating Fluidized Bed Technology, ed. P. Basu, Pergamon, Toronto, 263-272 (1986).

3. L. Reh et al. CFB Combustion: An Efficient Technology for Energy Supply and Environmental Protection, Inst. of Energy Symp. Ser. No. 4, VI-2(1-11) (1980).

4. B.M. Gibbs et al. Coal Combustion and NO Formation in an Experimental Fluidized Bed, Inst. of Fuel Symp. Ser. No. 1, London, D6(1-13) (1975).

5. M. Horio et al. Research and Development of NO_x Emission Abatement in a Fluidized Bed Coal Combustor in Japan, Proceedings of the Sixth Intl. Conf. on Fluidized Bed Combustion, Atlanta, 968-978 (1980).

6. T. Hirama et al. A Two-staged Fluidized Bed Coal Combustion for Effective Reduction of NO_x Emission, in "Fluidization", eds. D. Kunii and R. Toei, Proceedings of the Fourth Intl. Conf. on Fluidization, 443-450 (1984).

7. J.M. Beer et al. NO Formation and Reduction in Fluidized Bed Combustion of Coal, Proceedings of the Sixth Intl. Conf. on Fluidized Bed Combustion, Atlanta, 942-955 (1980).

8. T. Hirama et al. Nitric Oxide Emission from Circulating Fluidized-bed Coal Combustion, Proceedings of the Ninth Intl. Conf. on Fluidized Bed Combustion, Boston, 898-906 (1987).

9. J.R. Grace et al. Circulating Fluidized Bed Reactor Design and Operation, Sadhana, 10, 35-48 (1987).

10. R. Legros et al. Combustion Characteristics of Different Fuels in a Pilot Scale Circulating Fluidized Bed Combustor, Paper to be presented at the Tenth Intl. Conf. on Fluidized Bed Combustion, San Francisco, 1989.

11. H.A. Becker et al. Pilot Scale Trial on Atmospheric Fluidized Bed Combustion of a British Columbia Anthracite, Technical Report to EMR, Canada, QFBC. TR. 87. 4, 1987.

12. C. Brereton et al. Final Report on Contract 52ss.23440-7-9136, to EMR, Canada, 1989.

13. B. Leckner and L.E. Amand. Emission from a Circulating and a Stationary Fluidized Bed Boiler: A Comparison, Proceedings of the Ninth Intl. Conf. on Fluidized Bed Combustion, Boston, 891-897 (1987).

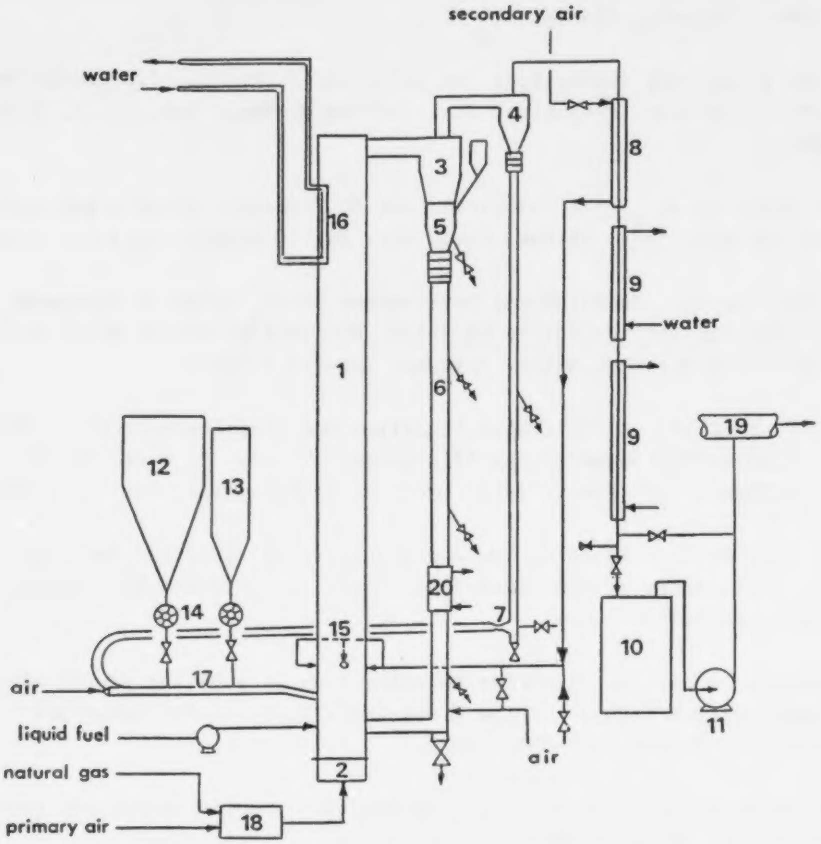


Figure 1: Simplified schematic diagram of circulating fluidized bed combustion facility (UBC) (10).

1. Reactor; 2. Windox; 3. Primary cyclone; 4. Secondary cyclone; 5. Recycle hopper; 6. Standpipe; 7. Eductor; 8. Secondary air preheater; 9. Flue gas coolers; 10. Baghouse; 11. Induced draught fan; 12. Fuel hopper; 13. Sorbent hopper; 14. Rotary values; 15. Secondary air ports; 16. Membrane wall; 17. Pneumatic feed line; 18. External burner; 19. Ventilation; 20. Calorimetric section

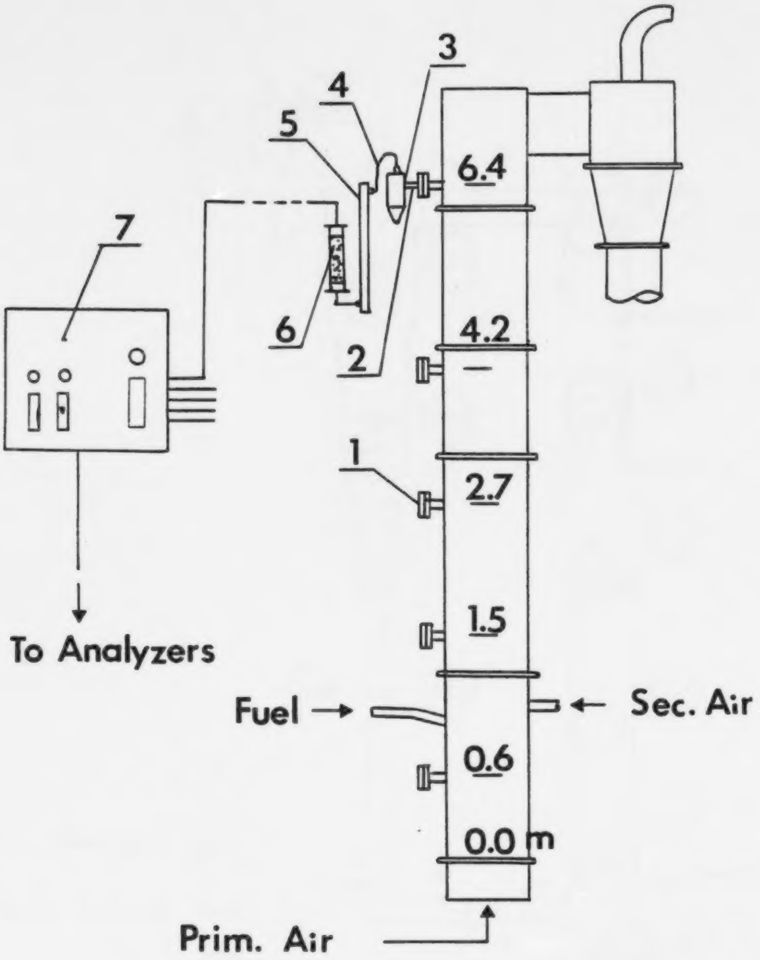


Fig. 2 Gas sampling system and vertical sampling positions:
1. Sampling port; 2. Gas sampling tubeextending into reactor;
3. Gas as filter; 4. Flexible stainless steel tubing;
5. Heat exchanger; 6. Drying tube; 7. Control panel and manifold
Note that only one of the five sampling trains is shown.

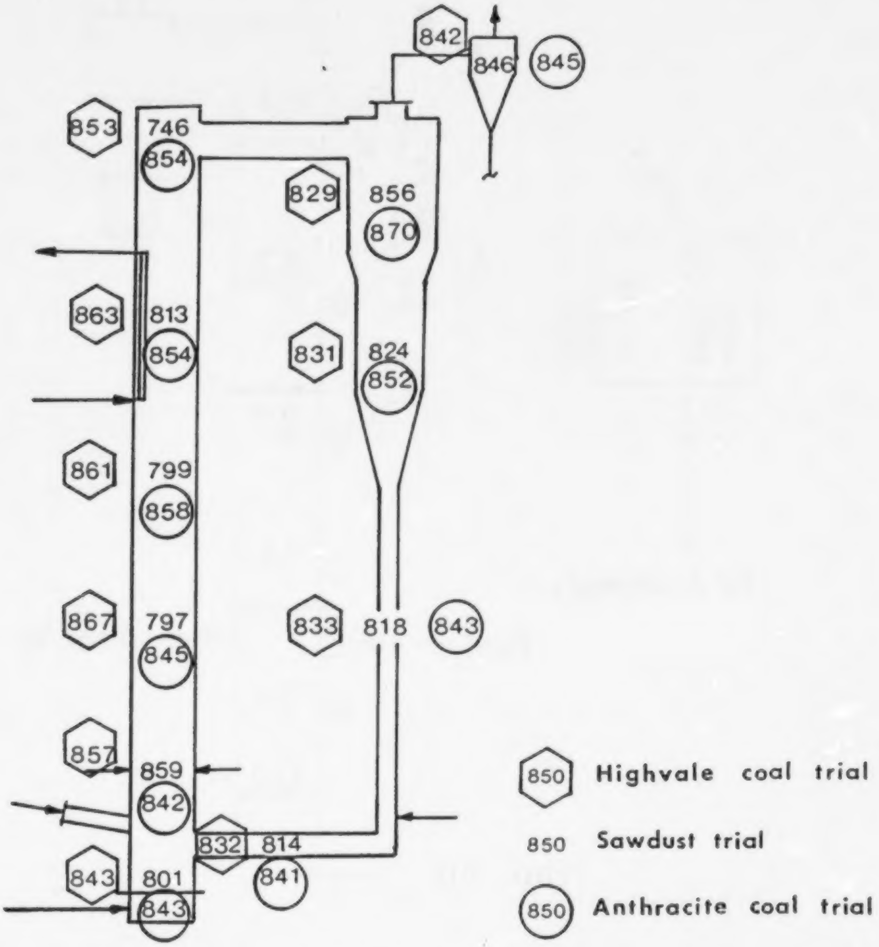


Fig. 3 Typical temperature profiles for various combustion trials (10).

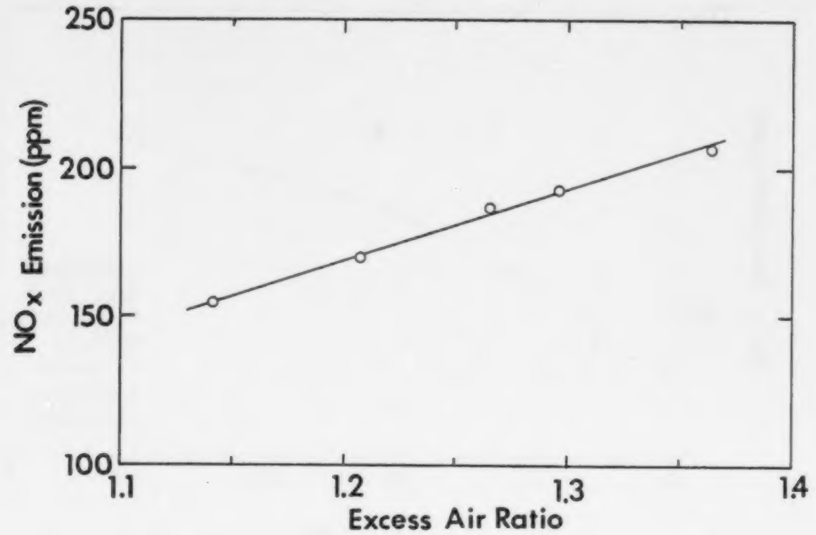


Fig. 4 NO_x emission vs. excess air ratio:
U = 8.0 m/s, T = 870°C, Secondary/primary air ratio = 1.0

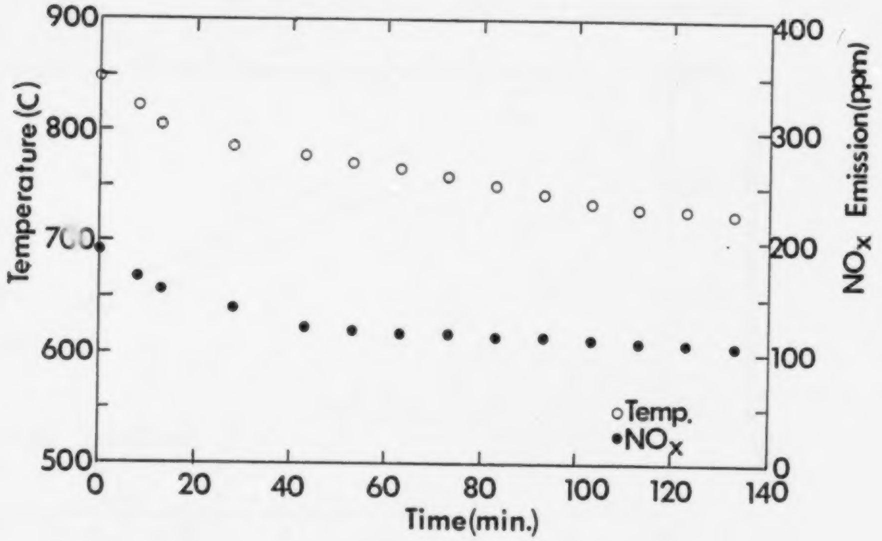


Fig. 5 NO_x emission and bed temperature vs. time after step decrease in fuel feed rate:
U = 6.0 m/s, Oxygen % = 9.5, Secondary/primary air ratio = 1.6

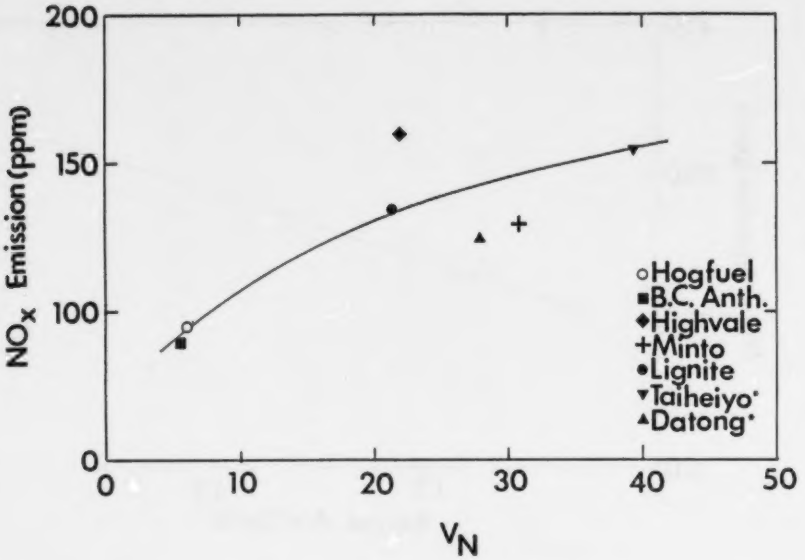


Fig. 6 NO_x emission vs. V_N (V_N = %nitrogen x %volatile in fuel)

*From reference (8) with conditions similar to those in this study.
Taiheiyo coal, N = 0.90%, volatile = 43.7%
Datong coal, N = 0.90%, volatile = 31.0%

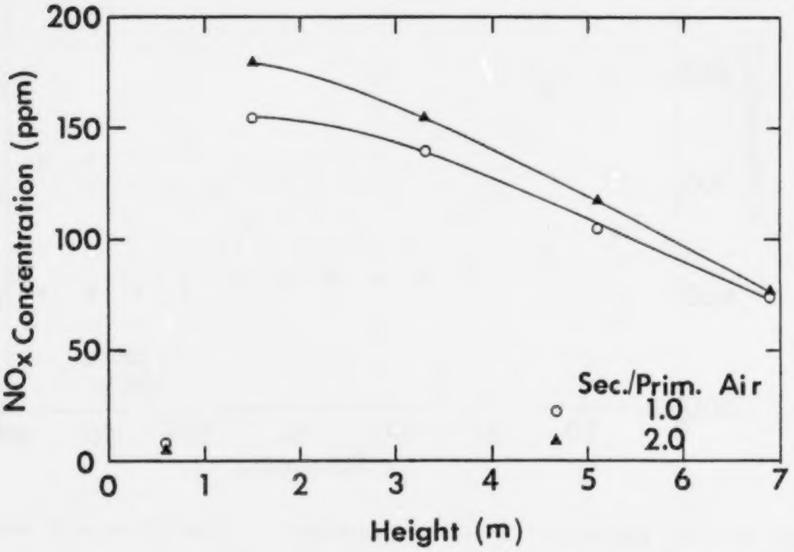


Fig. 7 Axial NO_x concentrations at the wall for two secondary to primary air ratios for lignite combustion:
U = 8.5 m/s, T = 870°C, oxygen in flue gas = 3.0%

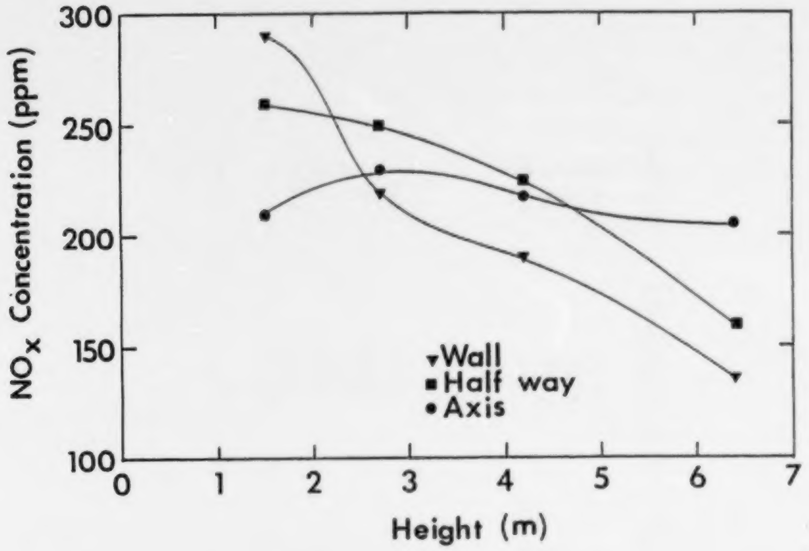


Fig. 8 NO_x concentration profiles for Minto coal combustion, U = 7.6 m/s, T = 890°C, Secondary to primary air ratio = 1.07, Ca/S = 3.01, oxygen in flue gas = 3.0%

Table 1: NO_x Emission from Combustion of Differen

	Minto Coal		Hogfuel		CANMET Pitch	
Superficial gas velocity (m/s)	7.0	7.8	7.1	7.6	7.5	7.8
Secondary/primary air ratio	1.0	1.0	2.2	2.6	0.56	1.07
Bed temperature (C)	865	870	830	825	847	895
Ca/S molar ratio	1.36	1.36	---	---	1.7	1.5
Sulphur capture (%)	72	70	---	---	78	83
Flue gas O_2 (%)	2.0	3.0	3.0	4.5	3.8	3.4
NO emission (ppm)	130	138	89	90	165	145

Table 2: Fuel Analyses (Wt%)

Proximate Analysis	Minto Coal	Hogfuel	CANMET Pitch	Highvale	B.C. Anthracite	Lignite
Volatile	32.9	60.9	67.7	31.0	6.6	35.6
Fixed Carbon	46.8	23.9	30.2	41.2	72.3	38.9
Ash	18.8	4.0	2.0	12.3	16.5	9.2
Moisture	1.5	11.2	0.1	15.5	4.6	16.3
Ultimate Analysis						
Carbon	64.8	52.8	86.2	52.1	72.5	51.4
Hydrogen	4.2	5.4	7.1	3.1	2.2	3.2
Nitrogen	0.7	0.1	1.1	0.7	0.9	0.6
Sulphur	7.2	0.2	2.8	0.2	0.5	0.6
Oxygen (by diff.)	4.1	36.9	1.0	16.1	2.9	18.6
Ash	19.0	4.6	1.8	27.8	21.1	25.5
High Heating Value (MJ/kg)	34.3	22.3	40.0	20.3	27.1	19.9

Table 3: NO_x Emission from Combustion of Anthracite
(3% Oxygen)

Superficial Gas Velocity (m/s)	Bed Temperature (C)	Sec./Prim. Air	NO_x (ppm)
7.7	872	1.0	80
7.8	875	0.5	80
7.9	884	2.0	97
6.0	874	2.0	86
6.2	882	1.0	90

Table 4: NO_x Emission from Combustion of Minto Coal
(3% Oxygen, sec./prim. air ratio = 1)

Superficial Gas Velocity (m/s)	Bed Temperature (C)	Ca/S	Sulphur Capture (%)	NO_x (ppm)
8.3	880	0	-	127
8.4	900	1.8	87.0	160
8.3	882	3.0	99.2	218

Session 7A

POST COMBUSTION NO_x CONTROL DEVELOPMENT

Chairman: C. Sedman, EPA

Design and Operation of the SCR-Type NOx-Reduction Plants at the Dürnrohr Power Station in Austria.

M. Novak
Verbundkraft Elektrizitätswerke Ges. m. b. H
Am Hof 6A
A-1011 Vienna, Austria

H. G. Rych
EVN Energie-Versorgung Niederösterreich Aktiengesellschaft
A-2344 Maria Enzersdorf, Austria

ABSTRACT

In 1986 the two hard coal and / or natural gas fired units of Dürnrohr Power Station in Austria, which are equipped with SCR-plants and with dry scrubbers started industrial operation.

The units have a power generating capacity of 405 MW and 352 MW. Construction started in 1981, in 1985 the decision was made to add full stream SCR-plants with 80 % removal efficiency. Until the end of 1988 the units have operated with SCR-plants 2254 and 9846 hours under intermediate load conditions.
The SCR-plants are of high dust type and they are equipped with plate type catalysts. The catalysts are situated upstream the Ljungström air heaters and the dry scrubbers. The engineering and the catalyst were purchased from a

Japanese manufacturer. Great care was taken to ensure the necessary load following abilities and to ensure conservation of the catalyst during the relatively long annual standstill periods.

Various performance tests were carried out, this paper reports about the results of two guarantee tests and two periodical tests. In addition sample catalysts were taken out of the SCR-reactors in order to study the quality changes of catalyst during operation time. The results of three sample catalyst tests indicate the good condition of the catalyst.

INTRODUCTION

Two Austrian Utilities, the Verbundkraft Elektrizitätswerke Ges.m.b.H. (VKG) and the EVN Energie-Versorgung Niederösterreich Aktiengesellschaft jointly erected the hard coal fired Power Station Dürnrohr between 1981 and 1986. The Power Station is located about 40 km west of Vienna. Each company owns and operates one of the two units.

An overall view of the power station in the final stage of construction is shown in figure 1.The boilers are single pass tower boilers, about 90 m high and they are equipped with low-NOx tangential burners, have a dry bottom and an empty downward fluegas duct between the economizer outlet and the airheaters. Hard coal from Poland with an average calorific value of 24.3 MJ/kg and natural gas can be used as fuels, both single or mixed.

Fluegas desulfurisation is performed by dry scrubbers with electrostatic precipitators in 3 parallel streams. To achieve better flexibility in endproduct sale, the flyash is separated by prefilters upstream the FGD.

At the hearings for the approval of construction of the power station in 1981 the authorities required the installation of NOx reduction facilities as soon as they were state of the art if ambient air conditions called for them.

After demonstration of the performance of the SCR-technology in Japanese power plants, VKG and EVN decided to install such plants in both units of the Dürnrohr Power Station in the beginning of 1985 after intensive preliminary studies. This decision was made regardless of the low NOx concentrations in the environment of the power station. The authorities required the SCR-plants to achieve a removal

Japanese manufacturer. Great care was taken to ensure the necessary load following abilities and to ensure conservation of the catalyst during the relatively long annual standstill periods.

Various performance tests were carried out, this paper reports about the results of two guarantee tests and two periodical tests. In addition sample catalysts were taken out of the SCR-reactors in order to study the quality changes of catalyst during operation time. The results of three sample catalyst tests indicate the good condition of the catalyst.

INTRODUCTION

Two Austrian Utilities, the Verbundkraft Elektrizitätswerke Ges.m.b.H. (VKG) and the EVN Energie-Versorgung Niederösterreich Aktiengesellschaft jointly erected the hard coal fired Power Station Dürnrohr between 1981 and 1986. The Power Station is located about 40 km west of Vienna. Each company owns and operates one of the two units.

An overall view of the power station in the final stage of construction is shown in figure 1.The boilers are single pass tower boilers, about 90 m high and they are equipped with low-NOx tangential burners, have a dry bottom and an empty downward fluegas duct between the economizer outlet and the airheaters. Hard coal from Poland with an average calorific value of 24.3 MJ/kg and natural gas can be used as fuels, both single or mixed.

Fluegas desulfurisation is performed by dry scrubbers with electrostatic precipitators in 3 parallel streams. To achieve better flexibility in endproduct sale, the flyash is separated by prefilters upstream the FGD.

At the hearings for the approval of construction of the power station in 1981 the authorities required the installation of NOx reduction facilities as soon as they were state of the art if ambient air conditions called for them.

After demonstration of the performance of the SCR-technology in Japanese power plants, VKG and EVN decided to install such plants in both units of the Dürnrohr Power Station in the beginning of 1985 after intensive preliminary studies. This decision was made regardless of the low NOx concentrations in the environment of the power station. The authorities required the SCR-plants to achieve a removal efficiency of 80% at fluegas temperatures above 310° C and the 8 hours average of the outlet NOx concentration expressed as NO2 to be lower than 200 mg/Nm3 (97.6 ppm). The NH3 slip was required to be below 5 ppm.

At the beginning of 1989 a new law came into force in Austria requiring by 1995 all existing power stations fired with coal must achieve NOx emissions lower than 97,6 ppm and if fired with gas lower than 73,2 ppm. These values are defined as 30 minutes average. The Dürnrohr power station already fullfills all these requirements today. By the way, more than one third of the thermal capacity installed in Austria, which is only 4000 MW, is already equipped with SCR-plants.

Until January 1st, 1989 Unit 1 was operated 2254 hours and Unit 2 9846 hours with the SCR-plants.

DESIGN AND LAYOUT OF THE SCR-PLANTS

The basic design parameters can be seen in table 1.

The ID-fans were already installed and would only be changable with significant costs. Therefore it was necessary to limit the pressure loss of the SCR-system. After intensive studies it was also decided not to change the airheater plates, which were delivered already. In the tender specification, the suppliers were asked to design the system for end of operating period flue gas conditions. The safety margins gained this way in our opinion are an important reason for the good system performance that was achieved. The contract for the SCR-plants was awarded to a consortium consisting of Babcock Hitachi Corporation (Japan) and Voest-Alpine (Austria). The plants are of High-Dust type and they are equipped with Hitachi plate-type catalysts. The technical data can be taken from table 2.

Description of the SCR-System

Working temperatures of the SCR-system are between 310 and 420° C. Because there was no space for a layout with reheaters downstream the FGD, the reactors were installed above the existing airheaters in an altitude between 50 and 90 m above plant zero. Due to the progress of construction the support structures of the SCR-reactors were built in different ways for both units. At Unit No.1, which was almost finished, a separated support bridge was built above the air heater building while the housing of the airheaters of Unit No.2 could be modified to support the reactor. Figure 2 shows this arrangement.
The horizontal inlet duct of the SCR-reactor was connected to the bend of the empty downward duct of the boiler. After a damper the ammonia injection grid and a mixing grid are located in the inlet duct. The flue gas goes through the reactor from top to bottom leaving at the outlet damper. The outlet duct is connected to the flue gas duct above the air heaters. The flue gas duct and SCR-reactor arrangement was modelled by Hitachi in a scale 1:20 to achieve a good fluegas velocity distribution and low pressure losses.

Since the boilers and flue gas ducts are hanging free in the boiler house and the SCR-reactors belong to a different static system, displacements of up to 180 mm may occur and the compensation and suspension system had to be sophisticated to keep low forces in the connections .

Most parts of the SCR-reactors are housed, except for the inlet damper which in due course gave trouble with the limit switches in winter.

Ammonia supply

Ammonia is supplied to the SCR-reactors from a common storage and vaporizing system with a pressure of about 1.9 bars and is diluted with 9000 m3/h of air extracted from the boiler house. The dilution air flow is constant over load.

The ammonia injection into the flue gas is carried out via 20 separately adjustable nozzle systems into a flue gas duct of 12 x 5 m. The total number of nozzles for each plant is 370. The most important part of initial startup was the proper balancing of the NH_3 distribution to achieve a uniform NO_x distribution at the outlet of the reactor.

Catalyst

The catalyst is arranged in 2 layers of about 2.0 and 1.5 m height in the reactors. The reactors are designed to hold 140 % of the initial catalyst volume. Before the exchange of layers additional catalyst will be loaded to compensate the decrease of activity during operation.

The catalyst plates consist of a plasma coated steel grid with the ceramic catalyst material applied to it. The plates are corrugated and assembled in boxes like air heater elements. The boxes are put together in blocks weighing about 1 or 2 tons. This block is the unit for handling, its size is about 1 x 2.3 x 1.3 m or 1 x 2.3 x 0.7 m. A system of hoists has been constructed for transportation on site. Figure 3 shows catalyst blocks during the initial loading of the reactors.

Above, between and below the catalyst layers the installation of soot blowers is possible. So far the soot blowers have not been necessary, it seems they will not be needed at all, because significant ash deposits on the surface of the catalysts, erosion of the inlet edges of the plates or clogging have not been observed. Only on some of the sample catalyst brackets, which are located about 1 to 2 meters above the layers and protrude about 1 meter into the reactor, dust deposits have been found, that clog the channels between the catalyst sample plates.

Bypass

Into the existing bypass duct of the boilers a damper was installed between the inlet and outlet ducts of the SCR-reactor. This damper is closed during operation, but during startup and shut down operation it allows operation of the boiler without gas flowing through the reactor. At startup the fluegas is led through the reactors when its temperature exceeds 100 C. NH_3 is injected above 300 C metal temperature into the reactor. The heating of the reactor does not elongate boiler startup operation, but because of the 300 C limit for NH_3 injection, the first 2 to 5 hours of boiler operation there is no NO_x removal by the SCR-system. The bypass helps to shorten the startup time of the plant, but it does not seem to be necessary to install a bypass if designing a new plant.

Catalyst Conservation System

Since alkaline flyash traces on the surface of the plates can react with the catalyst material in a wet environment, a dry conservation and heating system was installed. As Austria is primarily a water power country (about 70 % of the annual electric power production is made from hydro power stations), the thermal power stations have almost no operation in Summer. During these long standstill periods the air in the reactors is kept below 55 % relative humidity. The dryer system extracts air from the top of the reactor and injects dried air at the bottom. This system is equipped with a steam heater and is also used to heat up the reactor to 50° C before startup of the plant. As startup fuel is natural gas, this measure serves as a protection of the catalyst against condensation of vapour on the catalyst surfaces. The dryer system has given some trouble, because the dust in the reactor adheres to the dryer wheels and a high efficiency bag filter has to be installed to ensure a sufficient lifetime of the dryer wheels. The maintenance of the humidity control system and the hygrostatic switches is a labour intensive job because the switches used in air condition plants are affected by dust and humidity below 20 % which sometimes occurs. During standstill temperature and humidity in the reactors are continuously monitored.

Control System

The simplified line diagram of the control system of the DeNOx plants is shown in figure 4. The NOx concentration in the flue gas is measured before the reactor inlet and with a signal for the flue gas volume (calculated from the amounts of fresh air and fuel) the amount of NOx is calculated. Based on the given NH3/NOx molar ratio the NH3 injection is adjusted. In addition, due to the changing NOx concentration in the flue gas, a feedback signal from the NOx outlet concentration is superimposed which serves to adjust the molar ratio value in case of deviation from the desired removal efficiency.

Step functions and limiting functions make sure that even in case of transient conditions, for example mill failures, the injected NH3 amount does not increase too much. It was decided to permit lower removal efficiencies for short periods during transients to avoid breakthrough of NH3.

So far integration of the ammonia slip measurements in the control systems has not appeared to be possible or useful.

In the beginning, due to the buffer behaviour of the catalyst, adjustment of the control system was difficult. Finally it was possible to reach satisfactory results inspite of the system's high inertia. However, deviations from the set removal efficiency of 80% and outlet NOx concentration variations, for example from 110 to 240 mg/Nm3 - based on 150 mg/Nm3 in undisturbed operation - cannot be avoided, in case of a load increase from half to full load with simultaneous start of one coal mill. Within approx. 1 1/2 hours the system settles for steady values. If the control system is tuned more sensitive, it becomes instable.

Influence on Downstream Equipment

There was an intensive discussion about the deposition of sticky ammoniumsulfate compounds on the air heater plates, but so far none of these were found. This might be due to the low slip ammonia after the SCR. An abnormal increase of air heater pressure loss did not happen either, only in two cases sulfatic compounds on the cold end of the air heaters made washing necessary. These were caused by flyash and SO3 condensation due to very low inlet air temperatures.

The SO3 in the fluegas is removed completely in the dry scrubber FGD, the air heater outlet temperature is about 130 C, so far there were no signs of corrosion in the flue gas ducts.

The fresh flyash, collected by the ESP before the FGD, contains less than 50 ppm of ammonia and is sold to the cement industry without problems.

The performance of the dry scrubbers was not influenced in any way.

PERFORMANCE TESTS

Introduction

In the contract with the supplier of the DeNOx-plants Voest Alpine/BHK two guarantee tests beside the Taking Over tests are included. One test has to be in the middle (approx. after 6000 hours of op.) and the other at the end of the guarantee period of 12 000 hours of operation.

Beside the guarantee tests, periodical tests are carried out to check the condition of DeNOx-plants periodically. At periodical tests a reduced number of grid points are measured, compared to the guarantee tests. Periodical tests will be carried out yearly at the end of each operation period after guarantee time is over.
At the moment they give additional informations during guarantee time.

In addition to this, sample catalysts are taken out of the SCR-reactors in order to study the quality changes of catalyst during operation time. At this moment we can present the results of three sample catalyst tests which indicate the good condition of the catalyst.

The following part reports about the test results of Unit 2, because of the longer time of operation. The situation at Unit 1 is similar.

Guarantee- and Periodical Tests

The time schedule in table 3 shows the dates and the related operational hours of the DeNOx-plant at the Guarantee- and Periodical Tests.

At the Guarantee- and Periodical Tests the grid measurements had been conducted at the inlet and outlet duct of the SCR-reactors. The positions of the related cross sections are to be seen at figure 2.

There are 12 to 16 sampling nozzles at the side wall of the inlet and outlet duct of the SCR-plants, depending on the dimensions of each cross section. In order to get the actual grid of measurement points, 4 grid points at each sampling nozzle have to be chosen according to the Austrian standards (principle of area centre of gravity of rectangles equal in area).

For a well operating DeNOx-plant it is fundamentally necessary to have a good adjustment of the NH3 injection. The distribution of the NH3 injected at the inlet duct of the SCR-reactor has to be matched to the NOx and velocity distribution at the cross section of injection.

Before adjusting the trim valves it is necessary to know the flue gas condition at SCR-inlet and -outlet. Therefore the velocity-, temperature- and NOx distribution is measured first. Based on these measurement results the trim valves have to be adjusted until a uniform NOx distribution on the outlet of the reactor is obtained. After each readjustment of injection valves NOx has to be measured at selected grid points at the SCR-outlet.

In order to utilize fully the SCR-catalyst and the NH3, it is necessary to care about the distribution of NH3 injection. Keeping in mind the demands of local authorities and the necessity to protect the downstream components of the power station, the NH3 slip distribution at the SCR-outlet has to be examined. In our case the guarantee values, concerning NH3 slip, are less than 5 ppm for the average NH3 value and less than 6 ppm for each measuring point.

In order to calculate the SO2/SO3-conversion rate, SO2 and SO3 have to be measured at selected points at SCR-inlet and -outlet.

Up to now the Taking Over Test in February 1987 and the 1st Guarantee Test in April 1988 have been carried out. A detailed measuring programme was done because of the importance of these tests.

Table 4 demonstrates the measured flue gas components, the number of sampling points and the used measurement techniques at Guarantee- and Periodical tests.

Table 5 gives a survey of the guarantee values out of contract and the related measuring results of the guarantee tests. The measuring results are corrected or related to the design values of flue gas volume, flue gas temperature, NOx concentration (inlet), O2-content, and mole ratio NH3/NOx. To check the guarantee values the average values out of related grid measuring results are used. It is obvious that there was no problem to keep the guarantee values and there is no significant change in the DeNOx-plant condition, comparing the results of Taking Over Test and of 1st Guarantee Test.

The distributions of relevant flue gas components at the corresponding cross sections of flue gas ducts are an additional important criterion to estimate the condition of a DeNOx-plant.
Figure 5 explains the NOx- and flue gas velocity distribution at the SCR-inlet of the 1st Guarantee Test. It is remarkable to see the uniform NOx distribution beside the relative uneven distribution of flue gas velocity at the NH3 injection point.
Figure 6 compares the NOx- and NH3 distribution at the SCR-outlet of the 1st Guarantee Test. The well designed and adjusted DeNOx-plant is characterized by the relatively uniform distribution of NOx concentration and NH3 slip at the SCR-outlet.

To give a further description of the distribution of flue gas components, the relative standard deviations (standard deviations related to the relevant average values) of measured flue gas components at SCR-outlet are given in table 6.

The quality of NOx distribution at the SCR-outlet can be judged by comparing the relative standard deviations of the different tests. The NH3 slip distribution, depending on NOx distribution and adjusted NH3 injection, can be estimated as satisfactory knowing about the difficulties to influence it and the low absolute values.

Sample Catalyst Tests

At one wall of the reactor there are sample catalyst units, each three above, between and under the two SCR-catalyst layers.
Each unit contains 40 pieces of sample catalysts. The dimension of one piece is 100 x 100 mm.

At this time already three times sample catalysts were taken out of the DeNOx-plant Unit 2. Each time two pieces out of each sample catalyst unit were taken out. These 18 pieces of sample catalysts were sent to Japan for investigation at BHK laboratories. Therefore there are test results of three samplings available beside the analysis of original catalysts out of production.

In table 7 the time schedule of sampled catalysts as well as the related hours of operation of the DeNOx-plant of Unit 2 are given. The test items and methods of analysing sample catalysts are given in table 8.

There are two different ways to describe DeNOx-efficency out of sample catalyst test results.

One way is to compare directly laboratory test results of DeNOx-efficiency of different samplings without a direct connection to the actual DeNOx-efficiency of the real plant. To get comparable efficiency data, constant analysis parameters must be supposed.

The other way is to look at the relative activity which is based on the activity of the original catalyst. This is theoretically a good way to describe changes of catalyst activity with time. One problem is to determine the activity of original catalyst. It is possible to relate to the average value of efficiency out of the original catalyst test result during catalyst production with a relative high reproducibility. The other way is to store a sufficient amount of sample catalysts outside of the DeNOx-reactor in a suitable manner, in order to determine efficiency together with sampled catalysts in laboratory at each sampling. If the unchanged condition of the stored original catalyst samples with time is given, the described method to compare efficiency changes of catalyst with time is preferable because of having no influence of different analysing parameters.
In the Dürnrohr case the relative activity based on the average efficiency of original catalysts has to be calculated, because there are no stored original catalyst samples available. As described above we get uncertain values for relative activity because of the high reproducibility of the original catalysts. In some cases the value 1.0 is exceeded.

Figure 7 shows the efficiency graphs based on the sample catalyst test results at different times. The efficiency was detected at three different temperatures of the test reactor. There are no significant efficiency drops to be seen at all three temperatures.

At table 9 the additional test results beside the DeNOx-efficiency at the different samplings are listed. At the given measuring results there are no significant changes in the case of SO2 conversion, impact- and erosion resistance between the original catatalyst and the results of sampled catalysts. In the case of specific surface area, porosity and content of sodium and potassium there are some changes to be seen due to the influence of operation. The found measuring results are absolutly not critical due to the Japanese experience .

CONCLUSION

The SCR-plants of the Dürnrohr Power Station have already operated for two years. As it was described in this paper, the SCR-plants are in an unchanged good condition. There is no drop in removal efficiency and no significant increase in slip ammonia detectible, the surface of the catalysts is dust free and no erosion could be found.

The system operates together with the other components of the power plant without making trouble or affecting the downstream equipment. We hope, that it will stay that way.

Reproduced from
best available copy.

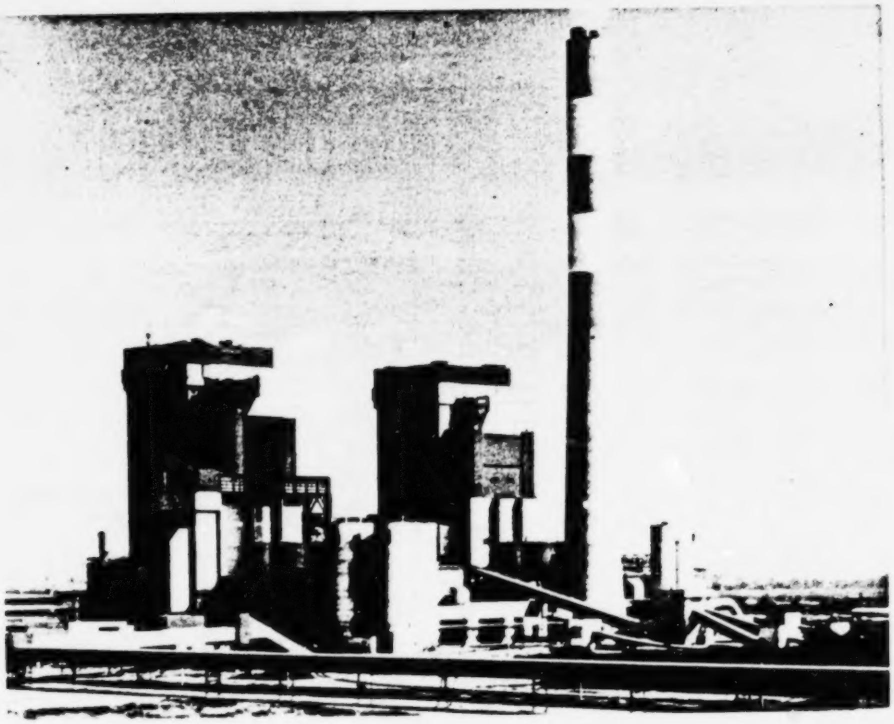


Figure 1. Overall View of Dürnrohr Power Station

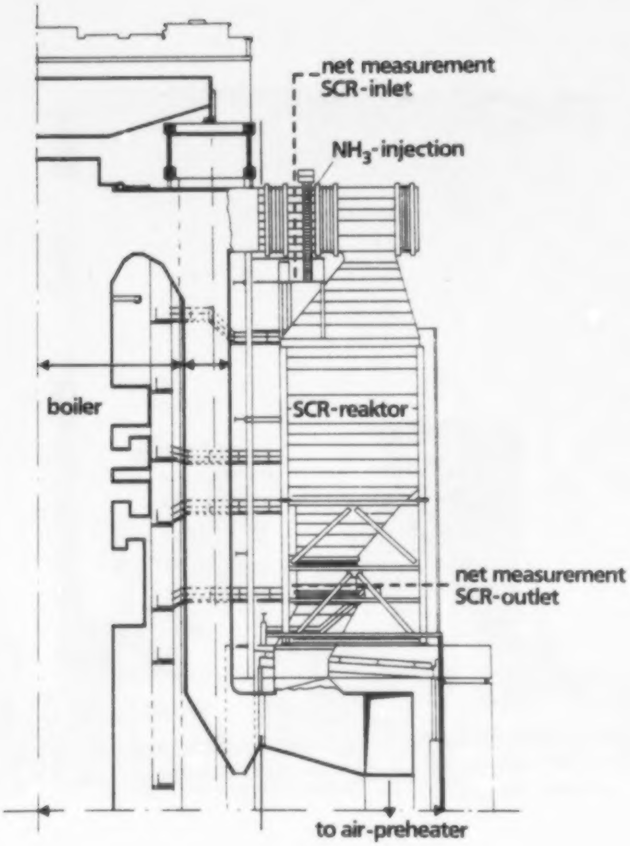


Figure 2. Dürnrohr Power Station. SCR-Reactor of Unit 2.

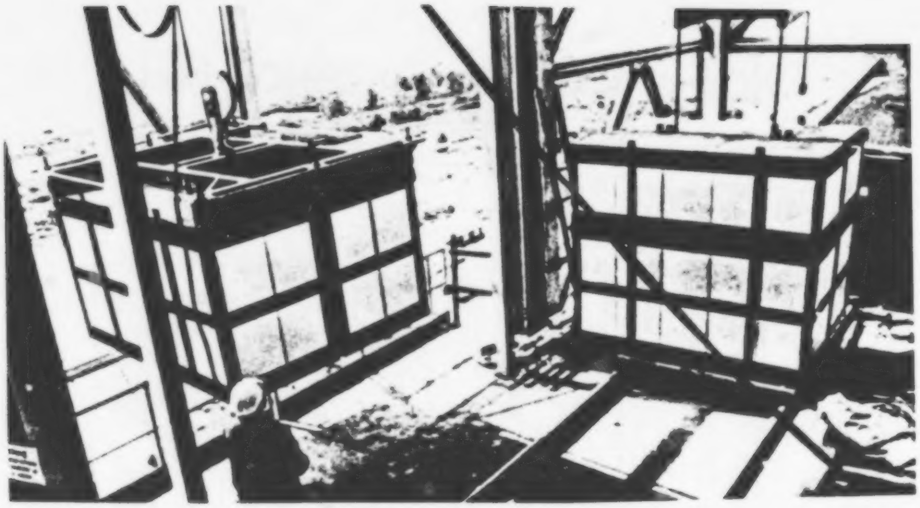


Figure 3. Catalyst Blocks of the SCR-Plant Dürnrohr Power Station.

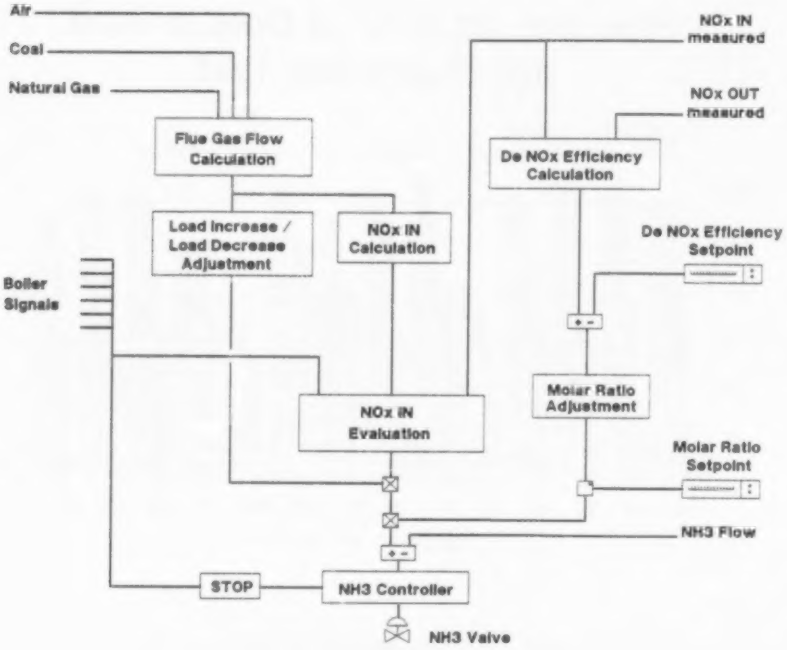
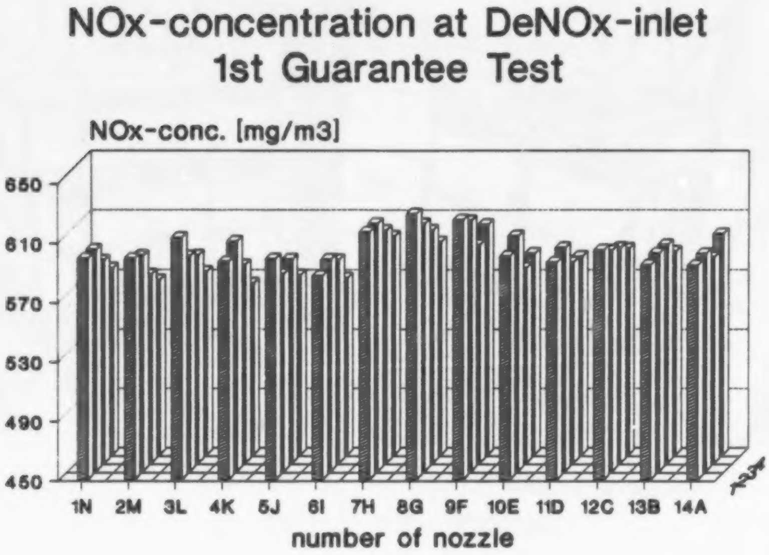


Figure 4. NH3 Control System of Dürnrohr Power Station. Simplified Line Diagram.



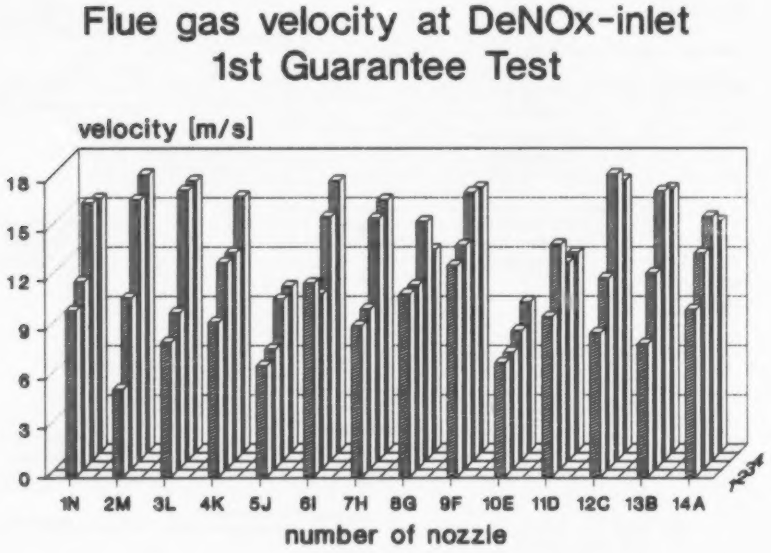
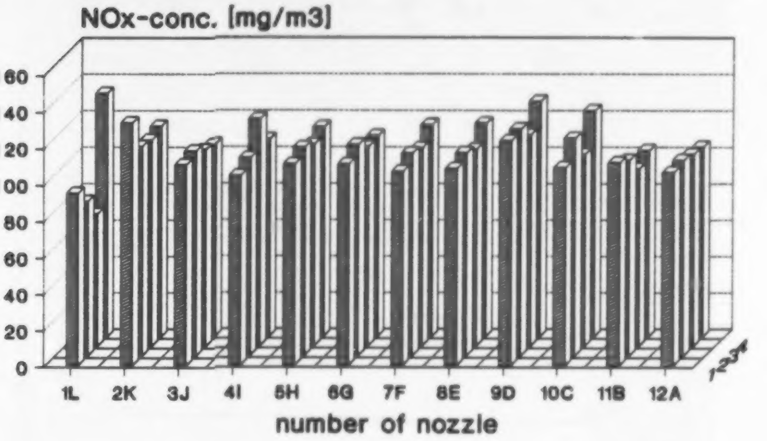


Figure 5. First Guarantee Test of Unit 2
Dürnrohr Power Station
NOx Concentration and Flue Gas Velocity Profiles
Inlet Duct of SCR-Reactor


NOx-concentration at DeNOx-outlet
1st Guarantee Test

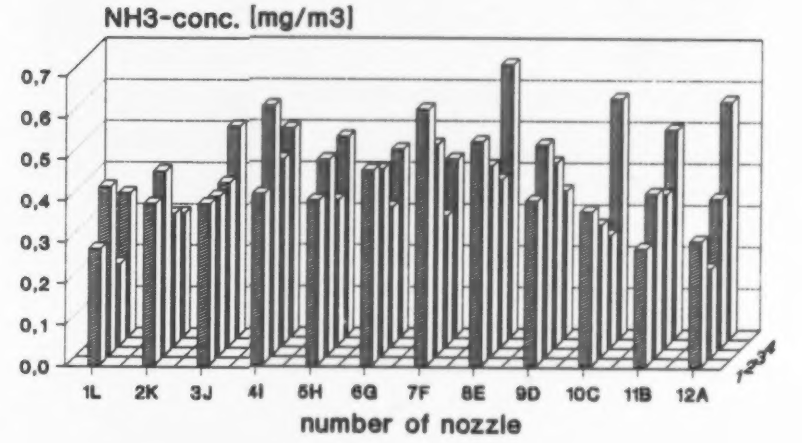

NH3-slip at DeNOx-outlet
1st Guarantee Test

Figure 6. First Guarantee Test of Unit 2
Dürnrohr Power Station
NOx-and NH3 Concentration Profiles
Outlet Duct of SCR-Reactor

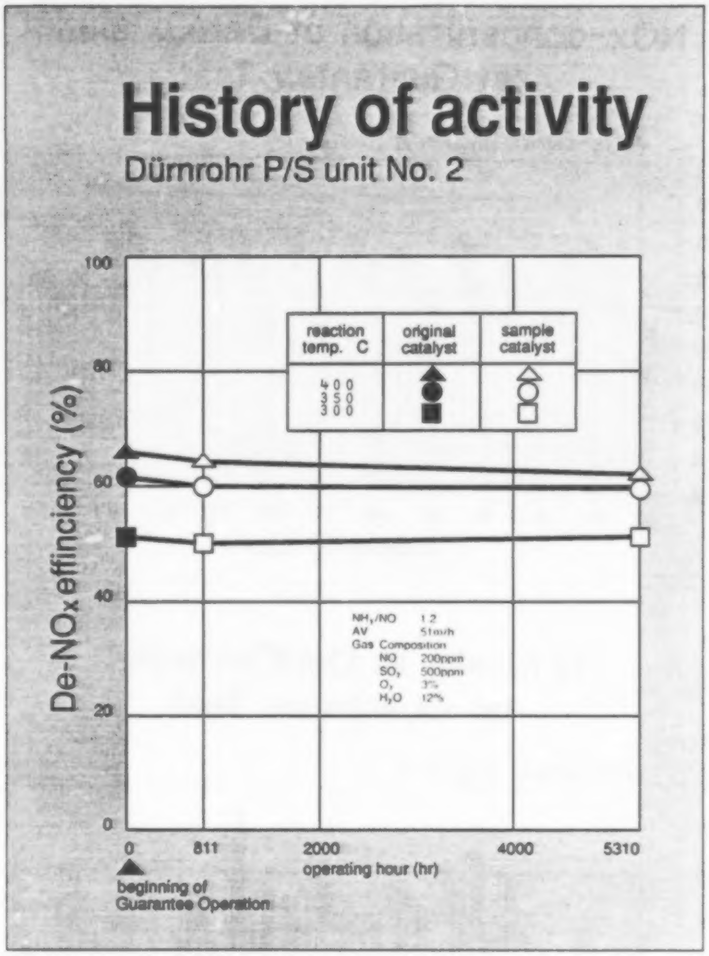


Figure 7. Sample Catalyst Test of Unit 2
Dürnrohr Power Station
DeNOx Efficiency of Catalyst Samples

Table 1

DESIGN PARAMETERS OF THE SCR-PLANTS
Dürnrohr Power Station

		Unit 1 VKG	Unit 2 EVN
Rated power	MW	405	352
Coal consumption	t/h	140	120
Nat.gas consumption	m3/h i.N.	92 000	79 000
flue gas flow	m3/h i.N	1210 000	1038 000
flue gas temp. after ECO	C	395	405
SO2 IN max	mg/m3 i.N	2300	2300
NOx IN (as NO2)	mg/m3 i.N	800	650
particulates IN	mg/m3 i.N	16 000	16 000
delta p SCR max	mbar	7	7.5
Cold starts per year		20	20

Table 2

TECHNICAL DATA OF THE SCR-PLANTS
Dürnrohr Power Station

		Unit 1	Unit 2
Removal efficiency	%	80	
NH_3 slip max	ppm	5	
SO_2/SO_3 conv.rate at 375° C max	%	1.5	
No. of catalyst elements (0,45 x 0,45 x 0,5 m)		5200	4800
Weight of catalyst	t	411	380
SV	h^{-1}	2270	
LV	m/S	4.9	

Table 3

SCHEDULE OF TESTS FOR UNIT 2
Dürnrohr Power Station

Kind of test	date of test	operational hours of DeNOx
Taking Over Test	Feb. 1987	0
1st Periodical Test	Oct. 1987	2011
1st Guarantee Test	April 1988	4280
2nd Periodical Test	Nov. 1988	6678

Table 4

MEASURING PROGRAMME
Guarantee- and Periodical tests
at inlet (1) and outlet (2) of the DeNOx- reactor
of Dürnrohr Power Station, Unit 2

flue gas component	number of points				method of analysis
	Guarantee T.		Period. T.		
	(1)	(2)	(1)	(2)	
NOx	56	48	28	48	chemilum. and NDIR
O2	56	48	28	48	paramagnetic
NH3	-	48	-	24	by wet process
SO2	6	12	6	12	NDIR
SO3	6	12	6	12	by wet process, japanese method
velocity	56	48	-	-	Prandtl tube
temperature	56	48	-	-	thermoelectric couple

Table 5

GUARANTEE VALUES AND MEASURING RESULTS
Dürnrohr Power Station Unit 2, coal firing

guarantee items	unit	guarantee value	Taking Over Test Feb.1987	1st Guarantee Test April 1988
DeNOx-efficiency	%	80 or more	81.5	81.5
NH3 slip	ppm	ave. 5 or less	0.32	0.63
SO2-conversion at 375 °C	%	1.5 or less	1.11	1.40
pressure loss	mbar	7.5	5.5	5.4

Table 6

NOx- AND NH3 DISTRIBUTION
Outlet Duct of SCR-Reactor
Dürnrohr Power Station Unit 2, coal firing

Flue gas component SCR-outlet	relative standard deviation in % at:			
	Taking Over Test	1st Period. Test	1st Guarantee Test	2nd Period. Test
NOx conc.	8.2	10.2	9.5	15.3
NH3 slip	35.0	-	24.4	-

Table 7

SCHEDULE OF CATALYST SAMPLING
Dürnrohr Power Station, Unit 2

	Date of sampling	hours of operation
1st sampled catalysts	June 1987	811
2nd sampled catalysts	May 1988	5310
3rd sampled catalysts	Sept. 1988	5310

Table 8

SAMPLE CATALYST TESTS

item	method
Catalyst activity (DeNOx efficiency)	A piece of catalyst is set in a reactor and the DeNOx-efficiency is measured, using a mixed synthetic flue gas at temperatures between 300 and 400 °C.
SO2 conversion to SO3	Three pieces of catalyst are set into a reactor where a mixed gas passes across it and SO2 concentration is measured at inlet and outlet of the reactor.
Specific surface area	The surface area of the catalyst is measured with N2-adsorption method (BET method).
Porosity	The pore volume of the catalyst is measured with the method of filling mercury into the pores by pressure.
Impact resistance	The weight difference of a piece of catalyst is measured after it is dropped ten times from 1 m height to a steel plate.
Analysis of accumulated material	Analysis of alkaline metals (Na and K by using AAS method).
Erosion resistance	The weight difference of a piece of catalyst is measured after 8kg of steel grit are dropped under a slope of 45 degrees from 500 mm in height.

Table 9

RESULTS OF SAMPLE CATALYST TESTS
Dürnrohr Power Station, Unit 2

Item	original catalyst	sampled catalysts		
	produced from Sept.85 to March 86	1st June 87	2nd May 88	3rd Sept.88
SO2 conversion [%]	av.:1.26 (0.62-2.20)	1.37	1.35	1.40
impact resistance [g/TP]	av.:0.11 (0.05-0.35)	0.07	0.11	0.10
erosion resistance [g/TP]	av.:0.13 (0.08-0.20)	0.17	0.16	0.14
specific surface area	1.0	0.929	0.921	0.911
porosity	1.0	1.036	1.184	1.114
sodium [%]	0.011	0.019	0.043	0.028
potassium [%]	0.002	0.011	0.051	0.023

DENOX CATALYTIC CONVERTERS FOR VARIOUS TYPES OF FURNACES AND FUELS
- DEVELOPMENT, TESTING, OPERATION -

L. Balling, D. Hein
Siemens AG KWU Group
Main Department Combustion
Hammerbacherstr. 12 + 14
8520 Erlangen, FRG

ABSTRACT

Different types of furnaces, such as dry bottom or wet-bottom furnaces, and different fuels, such as gas, oil and coal, where a further distinction must be made between hard coal, lignite, high-inerts coal and particularly sulphurous coal, call either for tailor-made catalytic converters or for a special plant design. This paper deals with development, testing and operation of honeycomb-type and plate-type catalytic converters in high-dust, low-dust or tail gas configurations.

Siemens/KWU is the only manufacturer which produces both honeycomb-type and plate-type catalytic converters and is thus able to look for the optimum technology for each individual application. In addition to catalytic converters for dry-bottom furnaces, a catalytic converter which is particularly resistent to poisoning by heavy metals was developed especially for wet-bottom furnaces.

This paper reports the most significant results obtained in laboratory tests and power plant operation.

1. INTRODUCTION

To date, the selective catalytic reduction (SCR) process has consistently proven itself for control of nitrogen oxides in power plant flue gases. Trouble-free and economic operation of this system in various types of power plants with various types of furnaces, fuels and operating conditions presupposes an optimized plant fitted with catalytic converters matched to the individual plant. To achieve maximum catalytic converter performance in the respective application, it is furthermore imperative that the manufacturing process and catalyst composition are tailored to plant requirements and, if necessary, supported by plant systems engineering measures. This is only achievable via a synthesis of knowledge of the catalyst behaviour which can only be provided in detail by those who develop and manufacture catalysts, power plant mode of operation experience (gathered by the utility and power plant contractor) and the resultant influence on the DeNOx plant. Furthermore, an extensive base of experience in process engineering is required, e.g. on those measures for achieving uniform gas and flow distribution that are essential to optimize DeNOx plant design and operation.

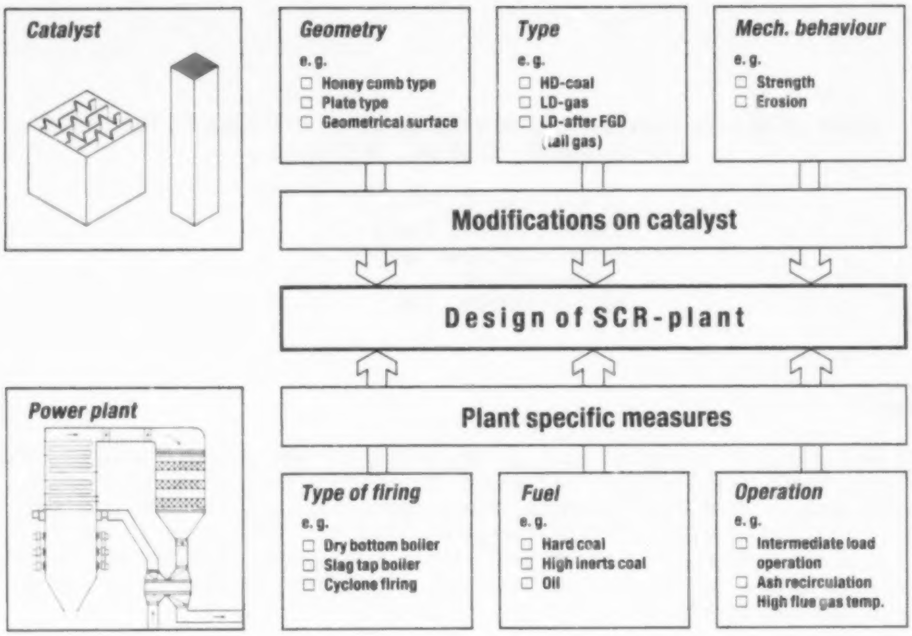


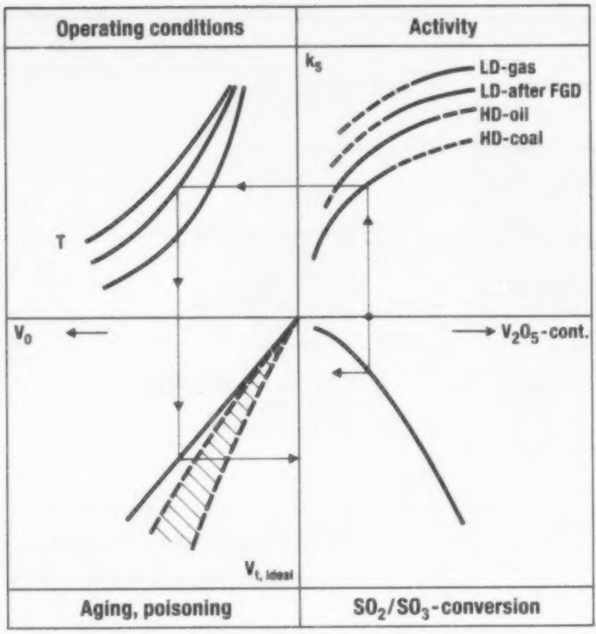
FIGURE 1: Design parameters for SCR-DeNOx-plants

Figure 1 depicts these interconnections in simplified form: special power plant requirements brought about by the type of furnace, fuel or mode of operation employed must be met by adjusting catalyst composition and manufacturing techniques. Further catalyst modifications, e.g. to increase resistance to poisoning, can increase the service life of catalysts, thereby substantially improving cost-effectiveness.

The following discussion presents examples to illustrate the demands placed on DeNOx catalytic converters and how problems can be effectively dealt with through targeted experimental investigations.

2. SOLUTION ON PROBLEMS ILLUSTRATED BY EXAMPLES

DeNOx reactor design, as shown in simplified form in Figure 2, begins with calculation of the catalyst volume V_0 which would be required at the beginning of operation from the characteristic data of the catalyst (e.g. the activity k_S, and operating conditions, which are defined primarily by flue gas volume and composition. By allowing for the aging process, during which catalyst activity drops from k_0 to k_t by the end of the guarantee period, $V_{t\ \mathrm{ideal}}$ the catalyst volume required under ideal conditions can be calculated. $V_{t\ \mathrm{ideal}}$ means that the unavoidable deviations from the ideal associated with actual operation have not yet been allowed for.



$$\boxed{V_{t,\,ideal} = \frac{\dot{V}_{FG}}{B \times k_t} f(\eta, \alpha)}$$

$$k_t = a \times k_0 \times e^{-\lambda t}$$

$$k_0 = k_S \times f_{O_2} \times f_{H_2O} \times f_T \times \ldots$$

k_S = Activity under standard conditions

FIGURE 2: Determination of the catalyst volume for an ideal reactor

These factors may have diverse causes, as shown in summary form in Figure 3, and must be allowed for by volume correction factors V in the design phase, e.g.:

A: A non-uniform flow distribution, caused, for example, by unfavorable duct routing, reduces NOx conversion.

B: Combustion of high-inerts coal produces high fly ash content flue gas; under such conditions, fly ash deposits and localized clogging are a threat.

C: Wet-bottom furnaces with their high temperatures release increased concentrations of catalyst poisons and simultaneously alter the structure of the ash particles such that fewer gaseous pollutants are bound to the ash. This increases the threat of accelerated deactivation.

D: The overall service life of catalysts and, consequently, cost-effectiveness, can be increased by plant design and, in particular by optimizing strategies for loading extra catalysts and replacing spent catalysts.

Selected examples are referred to in this presentation to illustrate specific problems, the solutions chosen and the results achieved.

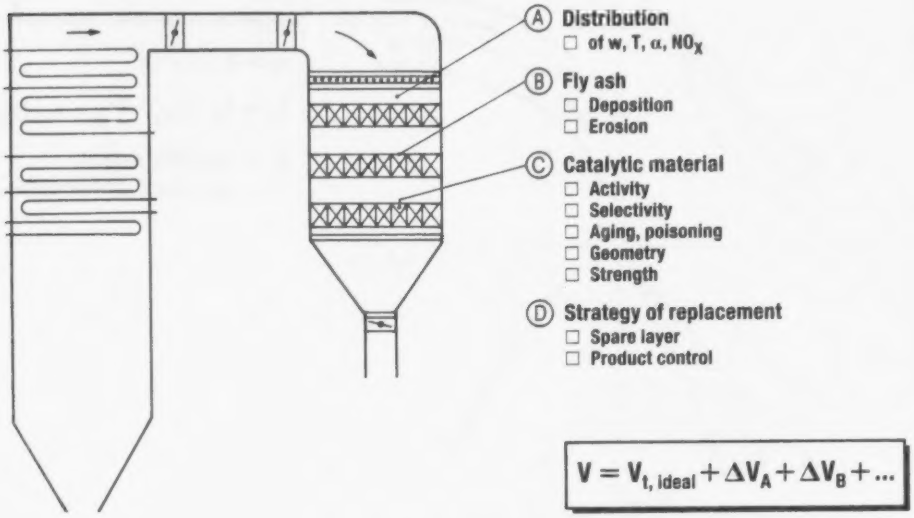


FIGURE 3: Reasons for an increased demand of catalyst volume

2.1 Effects of Non-uniform Flow Distribution

If the design of an SCR reactor is based on **one** value for flue gas velocity, flue gas temperature and stoichiometry, then it is equivalent to the ideal reactor. In reality, however, nonuniform velocity distributions occur, temperature striation is to be expected and the NO concentration over the reactor cross section may vary.

The deviations from uniform distribution always cause a reduction of NOx conversion and must be compensated for by increasing catalyst volume to achieve design performance.

Figure 4 shows a simplified reactor based on the assumption that three zones of equal size are present, one with conditions precisely equal to the overall average, a second with a positive deviation and a third with a corresponding negative deviation of the respective parameter.

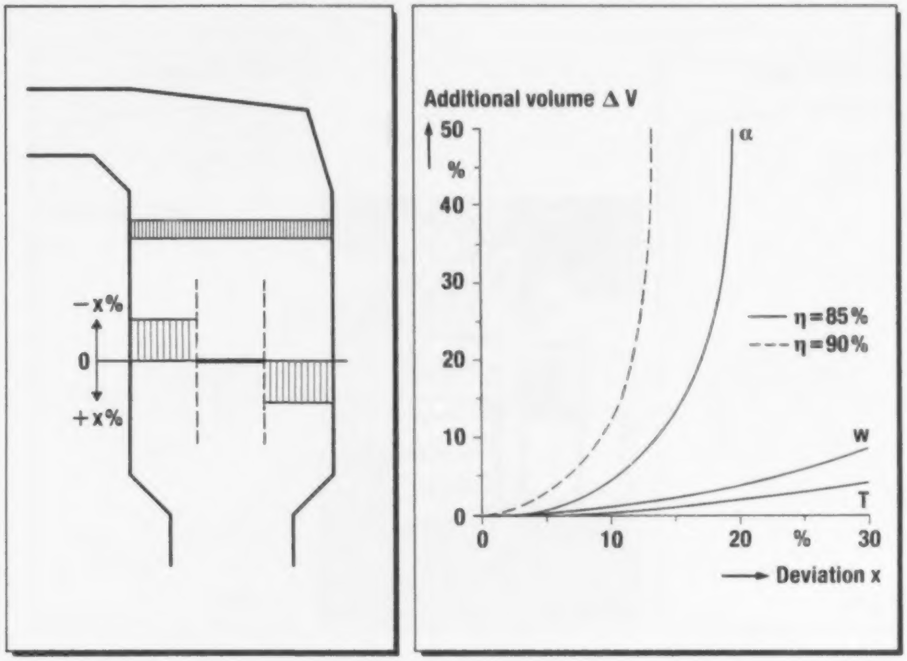


FIGURE 4: Effects of an unequality on the catalyst volume

Required volume correction factors calculated on the basis of these assumptions are plotted in Figure 4 as a function of the magnitude of the deviation from the parameters flue gas temperature T, flow velocity w and stoichiometry , i.e. the ratio NH_3 to NO_x at the reactor inlet. Design calculations perform individual statistical superposition of these deviations together with NO distribution so that a total of $3^4 = 81$ partial reactors are allowed for. The diagram clearly shows that the effect of temperature is relatively minor, and that even oblique flow requires a significant increase in catalyst volume but that large stoichiometry deviations cannot be accepted, owing to the magnitude of the requisite volume correction factor. This means, for example that NO distribution must be determined by field measurements during commissioning and NH_3 injection adjusted accordingly.

The effects of non-uniform distribution are highly dependent on the degree of NO_x conversion. The diagram is based on a typical conversion rate of 85 %. High conversion rates place stringent requirements on NH_3 distribution. At a conversion rate of 95 % and a stoichiometric deviation of ± 6 %, for example, NH_3/NO_x ratios > 1 occur. In such cases, local NH_3 breakthrough would occur, which could not even be prevented by vastly increasing the catalyst volume.

Due to their great economic importance, flow investigations are performed for practically all plants. Figure 5 shows a test setup and test results. It can be seen that the uniformity of velocity distribution can be significantly improved by positioning guide baffles in the reactor entry hood and additional flow straightener located upstream from the first reactor layer. The findings of distribution experiments on 1 : 15 scale models using air have proven fully transferable.

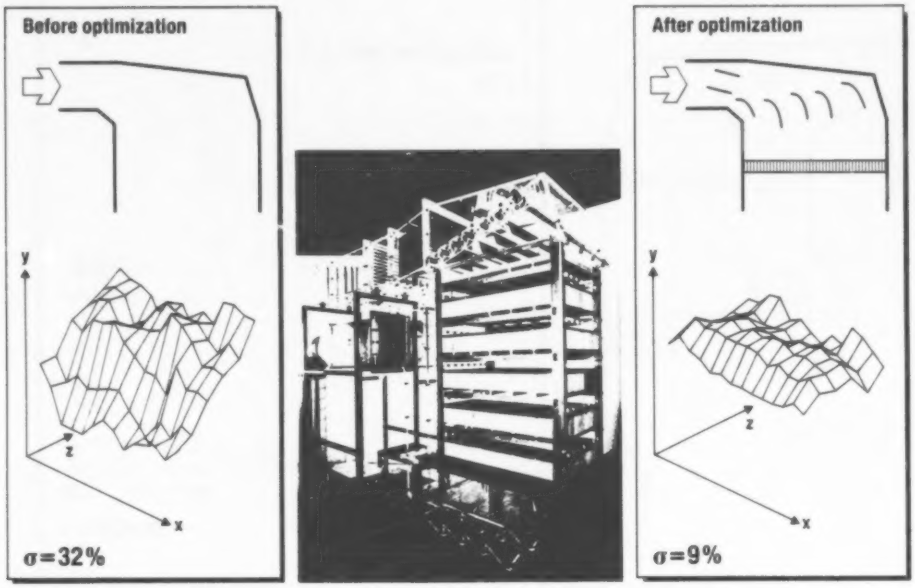


FIGURE 5: Flow tests to optimize velocity distribution

The following point are to be kept in mind when performing these design investigations:

- Simulation may not be restricted solely to the reactor, but rather must include ductwork upstream from the reactor, since the causes of oblique flow in the reactor are usually to be found here.

- Guide baffle arrangement must be such that no dust particle strictions occur which could cause jet abrasion.

- Zero-flow and reverse-flow zones are to be avoided, since they lead to buildup of fly ash deposits.

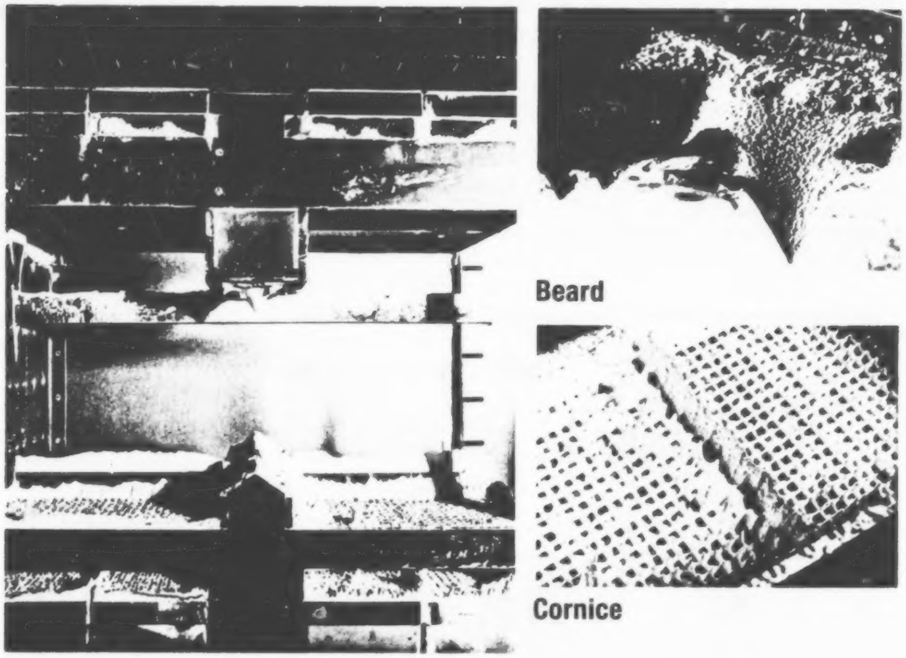
2.2 Prevention of Fly Ash Deposits and Erosion

There is a close connection between flow patterns and the formation of ash deposits on the catalyst surface. It has been debated whether a high fraction of coarse fly ash, which allegedly has self-cleaning effect, or a much lower concentration of fines causes partial clogging of the catalyst more rapidly.

Assumptions on the fraction of the catalyst cross section which will be clogged - and therefore are no longer available for catalysis - by the end of the service life must therefore be made during planning and design. This parameter is dependent on the structure and grain size spectrum of the fly ash and ultimately also requires a design volume correction factor. It must also be decided whether soot blowers are to be provided for cleaning the catalyst surface and, if so, at what interval they are to be actuated.

Special investigations focussing on dust deposition were consequently performed with the aim of

- clarifying the formation mechanisms of cornices (inlet side) and beards (flow exit side),
- recognizing the parameters which affect buildup of these deposits,
- proof-testing design measures to prevent these deposits,
- proof-testing on-line cleaning equipment,
- determining the limits of the use of fine grid honeycomb catalysts with regard to dust content and structure and
- investigating the differences in behaviour of honeycomb and plate-type catalysts with regard to dust.



Beard

Cornice

FIGURE 6: Deposition of fly ash

The test setup and typical results are shown in Figure 6. The most significant insights gained in these investigations can be summarized as follows:

- Clogging of cells is caused primarily by portions of cornices and beards which become detached.
- Coarse dust has a lower clogging tendency than fines (self-cleaning-effect).
- Rough catalyst surfaces are more conducive to build up deposits.

- The design is to minimize the size of stagnation zones, if necessary prevent them by using peaked hoods or shrouds.

- Reverse flow zones are to be minimized by the use of curved surfaces, shrouds and the like.

- Oblique inlet flow at angles > 15 ° are to be avoided due to the threat of erosion.

- Erosion processes can be predicted and, for the conditions in an SCR plant, can be controlled.

- The inherently flexible plate-type catalytic converter, as opposed to the absolutely rigid honeycomb element, is less susceptible to dust and at least must not be cleaned as frequently.

The results of these investigations provide guidelines which can be used for making a decision on whether to install plate-type catalytic converters or which honeycomb type can be selected without undue risk.

2.3 Deactivation by Poisoning

Catalysts age, that is, their activity drops during operation as a result of irreversible processes in the catalyst. Usually high deactivation rates were, however, measured in pilot plants in the high-dust region downstream from wet-bottom furnaces. Investigations have shown that arsenic oxide is the cause.

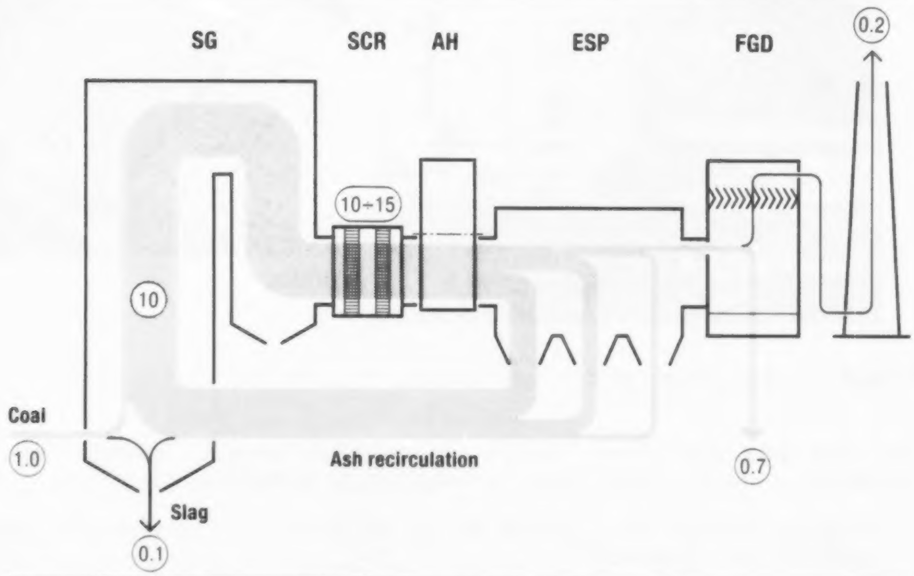


FIGURE 7: Arsenic mass flow at a slag tap boiler with ash recirculation

By extensive measurements in power plants and balance calculations of catalyst poison, we now know, that rapid deactivation is caused by arsenic oxide buildup during ash recirculation, as shown in Figure 7. Whereas the catalysts in a dry-bottom furnace plant are only exposed to the concentration contained in the fuel, wet bottom furnace ash recirculation and melting of fly ash in the combustion chamber increases the concentration to levels up to fifteen times as high. It is the gaseous fraction of arsenic which destroys the catalyst, and not arsenic bound to the ash.

The solution to this problem may lie in any of the following:

- Preventing enrichment, e.g. by complete or partial removal, particularly of highly laden fines

- Adsorption of gaseous As_2O_3 on fly ash or an additive upstream from the DeNOx reactor or

- Development of a catalyst resistant to arsenic.

Measurements of arsenic concentration in the individual sections of an electrostatic precipitator have shown that about 30 % of the total of arsenic agglomerated onto fly ash was precipitated bound to the fines fraction of fly ash, which accounts for only 18 % of the total amount of dust, in the final section of the electrostatic precipitatior. By partical extraction of only 18 % of the fly ash, arsenic concentration can be reduced by a factor of 2 - 3. This potential solution was not, however, pursued further, since the question of what to do with these fines is still open, rendering this concept unattractive.

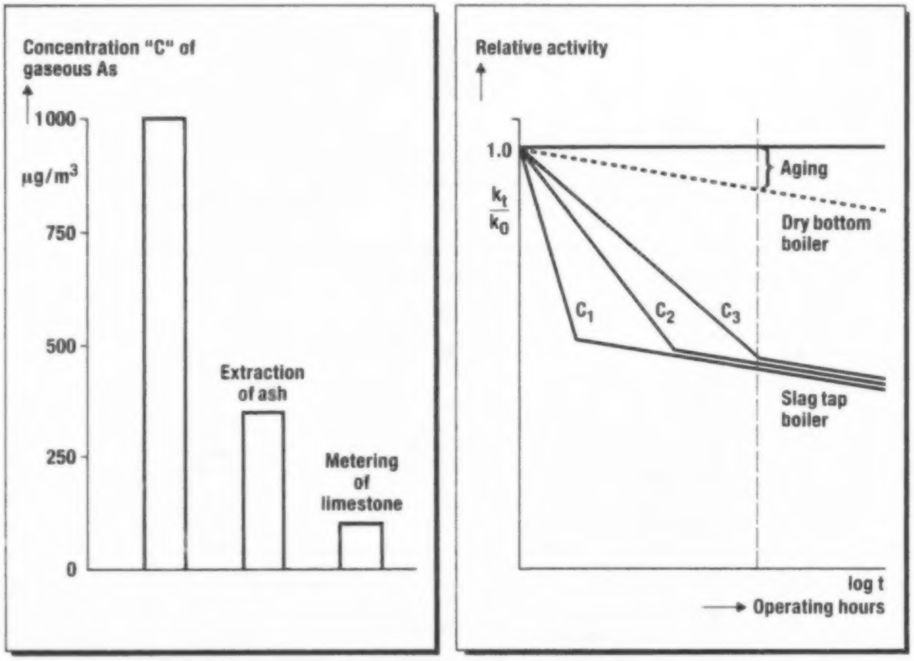


FIGURE 8: Effect of arsenic on the deactiviation behaviour of a special atalyst for slag tap boilers

Binding gaseous arsenic to a suitable additive supplied with the coal proved useful for two reasons. It is a well-known fact that when the fraction of crystalline substances contained in the ash is high, only very low concentrations of gaseous arsenic will be measured in the flue gas, even if the arsenic content of the coal was high. In a wet-bottom furnace plant where limestone was added to the coal to enhance slag flowability, it was also observed that no unusually high catalyst deactivation occured. For this reason, systematic measurements have been performed to investigate the effects of limestone dosing to bind arsenic. Results are given in Figure 8. It can be clearly seen that in this special case, admixture of limestone to coal reduces the concentration of flue gas arsenic from 1000 μg/m³ to less that 100 μg/m³. The reduction of arsenic deposited on catalyst specimens is particularly striking the effectiveness of this measure.

In spite of these positive results, we do not consider this measure alone sufficient, since the catalyst could suffer serious damage in a matter of hours in the event that limestone dosing is not available. Activity losses of 50 % were measured in a pilot plant in just 300 hours.

For this reason it seemed imperative to develop a catalyst which

- adsorbes less arsenic, i.e. has a lower affinity for arsenic than conventional dry-bottom furnace catalysts
- is less susceptible to arsenic poisoning.

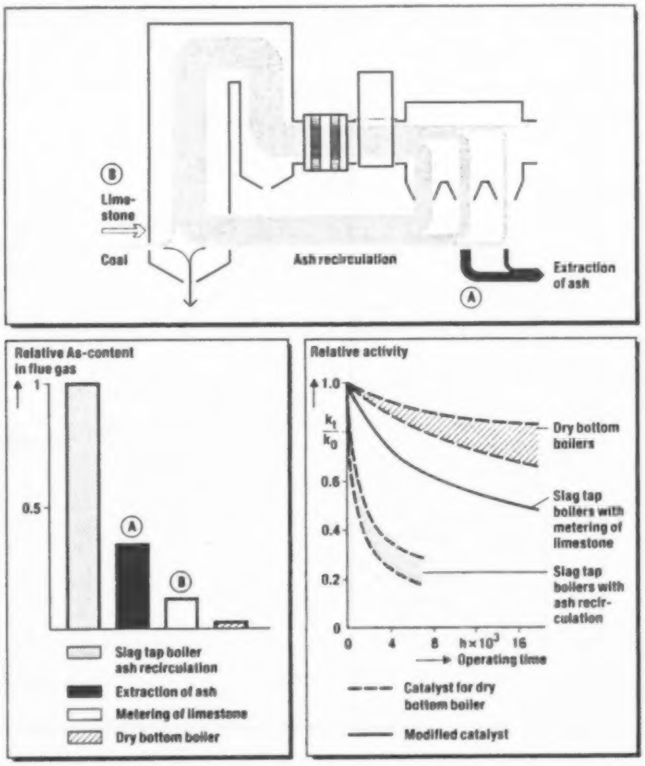


FIGURE 9: Effect of extraction of ash metering on lime stone

The success of this development, which combines both measures, is illustrated in Figure 9. This newly developed catalyst adsorbs only a limited amount of arsenic up to a saturation level which means that poison-induced loss of activity drops to a plateau. Normal aging occurs independent of this process, and the effects are superposed.

Reliability and economy can be maximized by using this newly-developed catalyst in conjunction with limestone dosing even when coal arsenic content, ash content and ash structure are unfavorable.

2.4 Effects of Design and Replacement Strategy Optimization

If the volume correction factors were minimized by the above mentioned measures, economy can still be significantly influenced by optimized strategies for addition of extra catalyst material and replacement of spent catalyst. This is illustrated by the reactor in Figure 10 which is fitted with catalyst elements in three layers. At time t_1 (guarantee period) the total activity of the reactor has dropped such that one layer must be replaced. The layer of fresh catalyst material increases the activity potential, which then decreases due to aging until a second layer must be replaced, and so on. In this example, over a period of 100.000 hours a total catalyst volume of 1600 m^3 is required, equivalent to four times the initial volume.

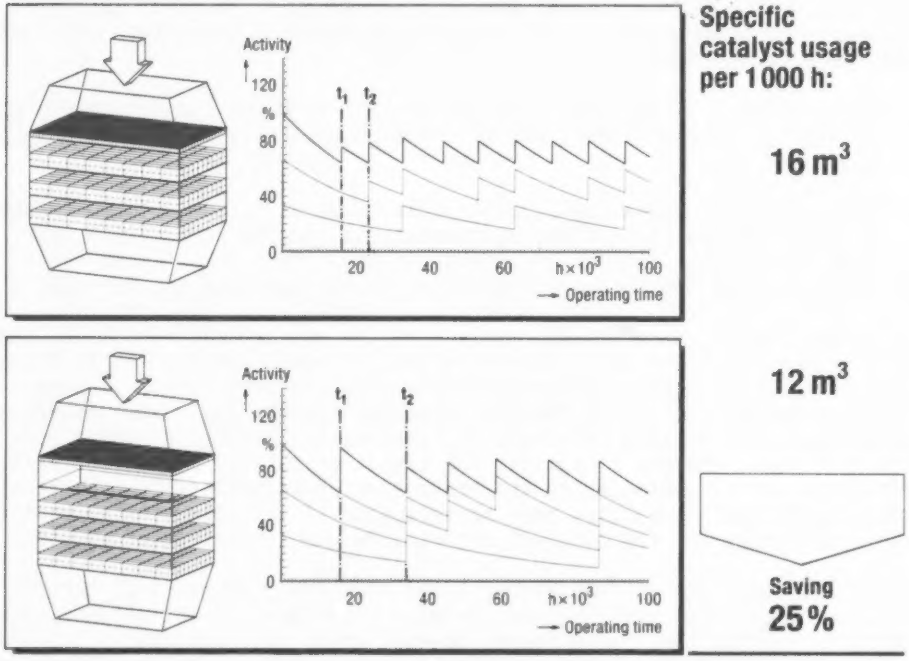


FIGURE 10: Improvement of catalyst Usage by strategy of change

Catalyst requirements are significantly more favourable when an additional reserve layer is provided in the reactor. An extra layer of catalyst material is loaded at the end of the guarantee period, which permits utilization of the residual activity of the three initial layers. Catalyst replacement is not necessary until time t_2. Over the same observation period, a catalyst volume of only 1200 m^3 is required, i.e. only three times the original volume.

After addition of the extra catalyst layer, reduced catalyst requirements are, however, partially offset by increased auxiliary power needs due to the greater pressure drop of flue gas flowing through four catalyst layers instead of three. This presupposes that the induced-draught fan system is designed to perform at this higher level. This example also demonstrates how inclusion of all these considerations during the planning phase can increase the catalyst usage factor.

Regular product monitoring employing catalyst specimens installed in the DeNOx reactor and laboratory measurements can be used to determine the exact times for addition of the extra catalyst layer or replacement in advance. This permits coordination with scheduled power plant maintenance activities.

3. EXPERIENCE GAINED IN COMMERCIAL POWER PLANTS

Experience gained at two commercial power plants is described below to illustrate to what extent the plant and catalyst-specific measures developed on the basis of the above design investigations have proven themselves under extreme operating conditions:

- Power plant A, fired with high-inerts coal in which fly ash concentrations as high as 50 g/m^3 occur, was fitted with catalytic converters on the high-dust side.

- Power plant B, where low-volatile coal requires firing at high temperatures, exhibits extremely high NO_x concentrations ranging up to 2,000 mg/m^3, therefore requiring a removal efficiency of about 95 %, was fitted with catalytic converters on the tail gas side, i.e. downstream from the FGD plant.

In power plant A, with its extremely high fly ash content - up to 60 tonnes of dust pass through the catalytic converter per hour - neither large deposits nor plugging nor erosion occured to date. A plate-type catalytic converter with increased pitch - and therefore greater flexibility - was installed. Module and reactor structure were designed with a minimum of surfaces which restrict flow, thereby minimizing the threat of cornice formation. Particular attention was also devoted to the prevention of transverse flow patterns. These plant design measures and the selection of a highly erosion-resistant modified binder for the catalyst material reduce the threat of erosion.

Initial inspections of the reactor after 1000 and 2500 hours of service detected no serious ash deposits. As with laboratory investigations, slight deposits in edge zones were found, however these are unavoidable and are of negligible significance. Erosion damage has not occured to date. The very positive results of commissioning measurements confirm the very favorable chemical and mechanical properties of the plate-type catalytic converter selected and the correctness of structural design measures implemented.

Power plant B ist characterized by an extremely high removal efficiency requirement of about 95 %. This efficiency, as explained in Section 2.1, can only be achieved without NH_3 break through when the NH_3/NO_x molar ratio is matched with extreme accuracy. For this reason permanent NO sampling grids were installed both upstream and downstream from the catalytic converter to permit appropriate NH_3 dosing even when NO concentrations fluctuate over a broad range.

Honeycomb-type catalyst having a high specific surface area of 751 m^2/m^3 with a pitch of 4,1 mm were installed. Catalyst activity was increased for example by adapting the pore structure to these particular operating conditions using a modified kneeding process (see Figure 2). Cell wall thickness was decreased to reduce SO_2-SO_3 conversion and pressure drop. Flow straighteners made of active catalyst material were installed above the first catalyst layer to enhance the uniformity of flue gas flow.

Commissioning test measurements showed that removal efficiency not only met but even exceeded the extremely high level required in a 14 x 20 m reactor cross section without NH_3 breakthrough. Measurements made downstream from the reactor and in the stack have not detected any NH_3 slip to date.

Even such extreme operating conditions, as demonstrated in the above plants, pose no problems which cannot be solved by targeted research and development focusing on matching the catalytic converter to the power plant.

4. CONCLUSIONS

When retrofitting power plants, the spectrum of requirements is by nature particularly broad, since the catalytic converter design must be tailored to existing plant conditions. A survey of the spectrum of application conditions is given in the list of references in Figure 11. References include nearly equal numbers of high-dust and low-dust plants. High-dust plant catalytic converters are subjected to flue gas temperatures as high as 430 °C. Wet-bottom furnace power plants operate with full ash recirculation and gaseous arsenic concentrations in the flue gas lie between 50 and 1000 $\mu m/m^3$. A catalytic converter installed downstream from a FGD plant which uses active char, however, is exposed to extremely clean flue gas.

Faced with this broad spectrum of requirements, Siemens AG KWU Group opted for manufacture of both types of catalytic converter, to be able to offer the best possible solution, both from the technical and economic standpoint:

- honeycomb-type catalytic converters with a high specific surface area, primarily for low-dust flue gas applications,

- plate-type catalytic converters with a lower suspectibility to deposits and erosion, mainly for applications with high-dust flue-gas.

The in-house base of experience available to the Siemens KWU Group - gained in the construction of power plants and design and development of catalytic converters along with the associated instrumentation - is needed to be in the position to offer complete package solutions, from fabrication to recycling, for the most diverse applications.

Type	Number of applicat.	Power [MWe]	Operating conditions	Catalyst type
High dust (after boiler)	3	1450	High grade coal	Honey comb
	2	622	High inerts coal	Plate
	3	1560	High operating temperature	Plate
	6	1220	Slag tap boiler	Plate
Low dust (after ESP or FGD)	8	3005	After wet type FGD	Honey comb
	4	588	After spray absorption	Honey comb
	1	700	After active char FGD	Honey comb
Refuse incinerator	1		Test facilities	Honey comb/ Plate
Industrial application	1		After glass furnace (mobile test facilities)	Honey comb/ Plate

FIGURE 11: Siemens-catalysts: references, operating conditions

ASSESSMENT OF JAPANESE SCR TECHNOLOGY FOR OIL-FIRED BOILERS AND ITS APPLICABILITY IN THE U.S.A.

Dr. Phillip A. Lowe, PE
INTECH Inc.
Potomac, MD 20854

William Ellison, PE
Ellison Consultants
Monrovia, MD 21770

Les Radak
Southern California Edison Co.
Rosemead, CA 91770

ABSTRACT

The Japanese have applied the Selective Catalytic Reduction (SCR) NOx (nitrogen oxides) control technology to 74 oil and gas-fired electric utility boilers. These applications have been made with specific limitations and restrictions imposed through siting, design criteria, and plant operating restrictions. Details of the Japanese experience were assembled through field visits and an updated literature survey. The results and conclusions developed during that study are presented in this paper. In addition, the relevance of this technology to meeting potential NOx emission objectives in the U.S.A. for oil-firing are discussed.

EXECUTIVE SUMMARY

It has been identified that in Japan the primary means for achieving NOx control for oil-fired utility boilers is by applying combustion modifications and by firing low nitrogen content fuels. Two thirds to three fourths of the obtained NOx control is achieved with these approaches. SCR is used as a final "polishing" step to remove up to an additional 70-105 ppm of NOx from the flue gas, when that is necessary to meet site-permitted conditions. SCR is thus a control designed to remove 30% or less of the uncontrolled NOx levels from gas and oil-fired utility boilers. Siting, design, and plant operating restrictions or limitations are used in order to assure the continued operation of the SCR system and a high availability of the utility plant. Such restrictions are imposed, even if they subsequently limit the NOx mitigation capacity of the installed SCR system.

Key Japanese design considerations include designing the SCR system for a maximum of 80% removal of the NOx entering the SCR reactor (but also planning to operate to achieve only 60-80% NOx reduction rates), and basing the SCR catalyst design on a titanium oxide formulation. Also, the design provisions included allowing for the formation and deposition of moderate amcunts of ammonium bisulfates, and including in the design the ability to conduct soot blowing or water washing to control those deposits.

The siting philosophy appears to be that the SCR system should be designed to fit the reasonably available space. This has resulted in the retrofit of 10-30% NOx removal system at existing plants.

Operational restriction are perhaps the most important considerations. The Japanese operated their SCR systems at reduced NOx removal rates (typically 60-80%) by restricting the amount of ammonia injected. This appears to be done with the full concurrence of the regulators. This approach further assures that operational problems and instrumentation inaccuracies will not restrict the plant power capacity or availability.

In terms of the application of the technology to U.S. utility boiler operations, important questions as to the impact of ammonia contamination of the flue gas desulfurization waste waters and equipment wash waters, and contamination of the boiler fly ash, and the selection of monitoring and control instrumentation averaging times need to be carefully considered because the Japanese experience indicates that these are unresolved problem areas. The Japanese have partially solved these problems by significantly restricting the amount of ammonia that is used in operations, and by not requiring the SCR system to be operated during low power, startup, and shutdown periods. Also, they specify a fixed NOx emission limit, as contrasted to a percent NOx reduction. At part load when the plant produces less NOx, this means that the SCR NOx removal rate can also be reduced.

INTRODUCTION AND BACKGROUND

The NOx from oil or gas-fired utility boilers is approximately 95% nitric oxide (NO) and 5% nitrogen dioxide (NO_2). The flue gas typically contains 2-6% oxygen (O_2), depending upon the firing conditions. It is known that a number of gases, such as hydrogen, carbon monoxide, and methane can reduce the NOx to elemental nitrogen (N_2). The Japanese developed the process using ammonia (NH_3) because it selectively reacts with the NOx while the other gases also readily react with oxygen. The governing equations for the ammonia-based technology are:

$$4NH_3 + 4NO + O_2 = 4N_2 + 6H_2O \qquad (1)$$

$$4NH_3 + 2NO_2 + O_2 = 3N_2 + 6H_2O \qquad (2)$$

Equation (1) has been verified in boiler operations, equation (2) is still a hypothesis. Also, these reactions require at least 1% O_2 to be present. The optimum temperature for these reactions is about 1000°C. Above this temperature a considerable portion of the ammonia is converted to NO, below this temperature the reaction rate is too slow. With a suitable catalyst present the reaction takes place at 300-400°C, a temperature range that is available in the flue gas system of a utility power plant.

If the reactions took place under ideal conditions, one mole of ammonia would be required to remove one mole of nitric oxide. This is stoichiometric chemistry. However, there are competing reactions and some of the ammonia is oxidized to water and NOx; and maldistributions of the NOx, oxygen, and ammonia mean that these components always are not together in the correct amounts to stoichiometrically react as they pass over the catalyst. Thus, in practice, one mole of ammonia reduces 0.80-0.97 moles of NOx.

Between 1977 and January, 1988, SCR systems were installed at 11 Japanese electric utility boilers fired with LNG and at 63 boilers fired with oil(2). The aggregate capacity represented by these installations is approximately 28,600 MW. A more meaningful measure of the impact of the SCR technology is to account for the installed NOx removal efficiency and the NOx concentrations that are actually processed by the SCR systems. In such a case, the aggregate capacity represented by those installations is equivalent to the SCR removing about 76% of the NOx from 100% of the flue gas from about 8,200 MW. Many of the retrofit applications were designed for 10, 30, or 40% NOx reduction rates, whereas applications at new plants are usually designed for 75-80% NOx reduction rates.

It is also important to realize that the specified % NOx reduction is for an "as new" plant. As the system ages during service the catalyst becomes less reactive, causing a reduction in the NOx removal rate or requiring a corresponding increase in the application of ammonia in order to maintain the NOx removal rate (with a corresponding increase in the inherent risks associated with not all of the ammonia reacting to reduce the NOx).

The Japanese philosophy(1,2,4,11,13,17) for implementing NOx control at electric utility power plants is based upon applying extensive combustion modification technologies and using fuels with low nitrogen content. This accounts for removing 200-300 ppm of NOx and assures that the NOx level that exits the boiler is in the 100-140 ppm (parts per million by volume) range(2,12,13). The SCR technology is used to further reduce the NOx concentrations by 10-80%, with the bulk of the applications in the 65-80% range. This accounts for removing 70-100 ppm of NOx. This important fact is often not clearly highlighted because the SCR system performance is usually referenced as a percentage reduction of the NOx that enters the SCR reactor, and not as the total amount of NOx removed or as a percentage reduction of the uncontrolled NOx emissions.

Plants located in crowded urban sites often apply 10-30% NOx reduction, as that is the most that can be achieved due to problems of physically locating the catalysts and duct work at the site. The 80% removal rate has been clearly stated(10,13,17) as being a realistic upper limit for SCR system operation at an electric utility plant. This is the result of the need to limit ammonia discharge to the atmosphere, the difficulties in obtaining greater reductions due to the inherent flow and concentration maldistributions in such physically large systems, and difficulties in measuring the discharge of the NOx and ammonia and those measurements' impact upon the ability to reliably maintain control of the plant.

Table 1 presents a summary of the Japanese boiler NOx emissions achieved for various combinations of combustion modifications. Table 2 indicates that SCR is only applied to about 15% of the system capacity at Tokyo Electric Power Company, a company with predominantly urban-sited power generation facilities. Many of the Tokyo Electric Power Company SCR systems only achieve 10 or 30% NOx reduction. Similar situations exist at the urban plants of Chubu and Kansai Electric Power Companies.

SCR SYSTEM DESIGN EXPERIENCE

Although the basic SCR system has remained relatively unchanged from the initial designs, the catalyst itself has been the subject of continuing improvement through research and development. Early utility operations identified problems that were amenable to correction through design changes. Such problems included: sulfur trioxide formation; ammonium bisulfate formation and deposition; catalyst poisoning by sulfur oxides and trace elements in the fuel; erosion of the catalyst by "hard" fly ash; and plugging of the catalyst by dust.

Table 1

Japanese Utility Boiler NOx Emissions For
Various Combustion Modification NOx Abatement Technologies(b)

FUEL	COAL	OIL	GAS
Fuel Nitrogen Content, %	0.7-3.0	0.1-0.5	0
TECHNOLOGY APPLIED	NOx EMISSIONS (in ppm)(a)		
No Control	500-800	250-400	200-300
Flue Gas Recirculation (FGR)	400-600	180-300	140-200
Two-Stage Combustion (TSC)	300-500	180-300	150-200
FGR and TSC	250-400	120-250	100-150
FGR and TSC and Low-NOx Burner	150-300	60-150	40- 80

Table 2

Tokyo Electric Power Company Oil and Gas-Fired Boilers Applying
Combustion Modification and SCR NOx Abatement Technologies(b)

METHODS OF COMBUSTION MODIFICATION GENERATING (MW)	NUMBER OF BOILERS	TOTAL CAPACITY
Flue Gas Recirculation (FGR)	15	1,860
FGR and Two-Stage Combustion (TSC)	12	5,290
FGR and Low-NOx Burners (LNB)	9	2,710
FGR and TSC and LNB	32	13,610
TOTAL	68	23,470
Boilers with SCR Also Added	8	3,540

Notes: (a) based upon 6% O_2 for coal, 4% O_2 for oil, and 5% O_2 for gas. To correct the values to a 3% O2 reference, multiply the values by 1.20 for coal, 1.059 for oil, or 1.126 for gas.

(b) from J. Ando, references 2 and 4.

The change to a titanium oxide-based catalyst resulted in a formulation that solved most of those problems in that it is resistant to sulfur oxide poisoning, and it does not oxidize sulfur oxides to the trioxide form. Without the trioxide present, ammonium bisulfate will not form. Newer designs include titanium with molybdenum and tungsten oxides, and they are reported to be even more resistant to the formation of sulfur trioxide.

In addition, flow straighteners to reduce flow maldistributions at the SCR reactor inlet, flue gas velocity limits in the catalyst region, and the use of parallel flow geometries for the catalysts helped control erosion and plugging problems. Extensive flow modeling is used to guide the design of the ammonia injection system. The designs include multiple rows of catalyst sections, and the amount of ammonia injected is also restricted in acknowledgement that up to 2% of the flue gas can bypass a row of catalyst blocks by passing through the spaces between the blocks. The limiting of the amount of excess ammonia reduces the duty on the catalyst and reduces its potential to produce bisulfates. The result has been a more rugged and longer life catalyst, but that trade off solution also has lowered, by 10-20%, the amount of NOx reduction that can be achieved in actual operations.

These changes have been made with the following basic design conditions and approaches retained. The catalyst operation is still in the 300-400°C range (recent designs have been in the 300-350°C range), and the catalyst high NOx reduction activity has been retained. The ammonia injection and control system is stable and responsive. The injected ammonia is vaporized and diluted with a carrier gas to a 5% ammonia concentration before it is injected into the duct. This is well below the ammonia flammability range in air of 16-25%. Blocks of catalyst are stacked inside the SCR reactor, but room is left for the addition of test coupons and additional catalyst blocks if that should prove necessary. The test coupons are examined during the annual plant inspections to help identify incipient problems, so that corrective action can be taken before a difficulty becomes a major concern.
The Japanese design strategy assumes that a moderate amount of ammonium bisulfate deposits will form and it recognizes that the deposit is highly corrosive (and thus special materials should be selected for those elements on which it could deposit), but that it is removable by soot blowing and water washing. Where high particulate loads are anticipated, they use a vertical downflow through the catalyst section. Otherwise, they prefer horizontal flow through the catalyst section because that results in less expensive duct work.

SCR SYSTEM SITING EXPERIENCE

The SCR system for a utility gas or oil-fired boiler is a large system, about one half to two thirds the size of a flue gas desulfurization unit that might be applied to the plant. For a system designed to treat the flue gas from a 250 MW plant, the basic SCR catalyst housing would be a structure about 30 feet square and about 50 to 70 feet high. The catalysts themselves could weigh as much as 400 tons, depending upon their formulation and the base material selected.

Of special concern is the retrofit of an SCR system at a site that had not initially planned for and provided space for its installation. The Japanese regulatory philosophy(7) on retrofit siting is basically that the SCR should be designed to fit into the reasonably available space. At crowded urban utility sites, such as in Tokyo, this has resulted in the installation of SCR reactors that are designed to remove 10-30% of the NOx entering the catalyst reactor, as compared to the 80% removal rate typical of new sites that can accommodate those larger facilities. Also, SCR retrofits cost 40-60% more(4,10) than do installations at new electric utility plants.

In 1980(7) site visits were made to discuss and to observe the SCR systems installed by retrofit at: Chugoku Electric Power Corp.'s Kudamatsu Station Unit 2 (375 MW); Chubu Electric Power Co.'s Chita Station Unit 4 (700 MW) and Nishinagoya Station Unit 6 (500 MW); and Kansai Electric Power Co.'s Osaka Station Unit 4 (156 MW) and Sakaiko Station Unit 6 (250 MW).

A summary of the findings of that study is: 1. The plants all applied combustion modification technologies in order to lower the boiler NOx production. The SCR systems were designed to operate at about 80% NOx reduction. 2. There was ample space available at each site for positioning the SCR unit without the need to relocate major equipment items such as air preheaters, fans and the exhaust stack. 3. There was a minimal need to modify existing foundations and steel structures to support the weight of the SCR system components. 4. At part load operating conditions the regulators required a constant NOx emission limit (ppm) rather than a constant NOx removal percentage rate. This effectively required less NOx reduction at part loads when the plant NOx emissions are reduced compared to full load operation. 5. Minimal relocation of underground utilities was required and new electrical transformers were not required. 6. Boiler structural modifications to meet new pressure conditions were not required. 7. Flue gas reheat systems were not required. 8. The design for boiler implosion prevention was not required.

SCR SYSTEM OPERATING EXPERIENCE

The early experience(1,2,3,4,5,9,14,17,19,20) with pellet (spherical shaped) and tubular geometries used for forming the SCR catalyst sections, along with the actual plant operations, identified a number of generic or repetitive problems. These included: 1) ammonium bisulfate formation and its subsequent deposition on the catalyst itself, termed "masking", and on the downstream equipment. It has been found(2,4,7,11,13,17) that: ammonium bisulfate deposits occurred on the ammonia injection nozzles, the SCR catalyst, the air preheater, the induced-draft booster fan, and the gas-to-gas heat exchanger; 2) catalyst poisoning by sulfur oxides and other constituents in the flue gas occurred; 3) catalyst plugging by fine particle dust occurred; 4) sulfur dioxide conversion to trioxide followed by bisulfates formation occurred; 5) catalyst erosion by hard particles in the fly ash occurred (this was principally a problem in coal-fired plants); and 6) NOx and ammonia measurement instrumentation inaccuracy and low durability (or high maintainability) was experienced.

Extensive development activities for improvement of the catalyst formulation and operational changes were taken in order to mitigate those problems. The status of these efforts is:

1) Bisulfate formation and deposition problems. The Japanese attribute the design change to titanium and vanadium-based

catalysts as the single most important catalyst development for controlling this problem. However, this change does not remove the sulfur, so additional operational changes were required. The single most important operational change was attributed to being the reduction of the amount of injected ammonia (even if it reduced the overall NOx reduction). By keeping the excess ammonia (e.g., the ammonia slip or bypass) to less than 5 ppm (and preferably less than 3 ppm) the rate of bisulfate production is small enough that the resulting deposits can be controlled by soot blowing and water washing. Another operational change was to reduce the catalyst operating temperature to less than 350°C to reduce further its oxidation potential (but remaining above 300°C to restrict bisulfate formation). The actual operating temperature has been found(4) to be a function of the inlet concentrations of the sulfur oxides and ammonia and the sulfur dioxide oxidation potential of the specific catalyst being used.

2. The catalyst poisoning problems were corrected by converting to the titanium-based catalyst material, which is more resistant to poisoning by sulfur oxides. Operational changes such as tighter controls on permissible fuel trace elements, such as alkali and arsenic compounds, help eliminate these problems. Catalyst samples are tested during the annual plant inspection. Those test results can give an early warning of any significant loss of catalyst activity.

3. Correction of the plugging of the catalyst pores with fine particle dust (particles less than 1 micron in size) was accomplished by soot control operational measures such as soot blowing and water washing. In addition, the use of parallel flow catalyst geometries further reduced the opportunity for fine dust to reach the catalyst surface. The utilities are restricted from using "combustion enhancing additives" and cleaners because they have been found(4) to contribute to the fine dust problem. The covering or fouling of the catalyst surface with bisulfates is similar to this problem, but the dust deposition is considered as a "blinding" problem, while the gross covering by bisulfates is considered as a "masking" problem. The difference is that soot blowing, washing (some catalyst suppliers do not allow washing of their catalysts), and volatilization by heating can remove the masking problem, but they are not effective operational mitigation procedures for the blinding problem.

4. The steps taken to limit the formation and deposition of bisulfate salts essentially corrected the problem of forming sulfur trioxide.

5. Erosion control was obtained by a number of design changes related to flow geometry and flue gas velocity.

6. The instrumentation problems remain an open issue(2,6,8,11,13,15,16). In general, their long response times and inability to obtain a reading in the ppm range that represents the conditions in a duct that is meters in diameter are difficult problems. The control of the SCR system is often not based upon actual instrument readings of the NOx and ammonia levels, but is based upon using calculated values. The instrument readings of either of these concentrations can be used to trim the control setting, but they may not be accurate enough and may have too slow

a response time for any significant control other than steady state or static operational conditions. Also, the maintenance effort for the instrumentation is considerable(6,8).

The main SCR concern during startup and shutdown operations is the potential for damaging the catalyst due to soot or moisture(17). The Japanese do not operate their SCR systems during these periods and during low power operations (e.g. power operation between 0-40%, depending upon the plant being considered).

The SCR system control is strongly tied to instrumentation issues. The most obvious(11,12,13) operational control strategy has been to design the SCR system for operation at 80% NOx removal and to frequently operate it at lower removal rates by injecting less than the design feed rate of ammonia. This is done, of course, to limit the ammonia slip and to thus assure that bisulfate problems do not occur. It also reduces the dependency of the operations upon accurate emission measurements, since all the ammonia should be consumed and the NOx emission level that results appears to be acceptable to both the utility and the regulators. Another way to look at this is that, in effect, additional catalyst material, above that which is needed for operating conditions, is installed. This contributes to the long catalyst lifetimes actually experienced (in oil and gas service catalysts are warranted for 2 years, yet they last for 4 to 8 years for oil and 7 to 11 or more years for gas-firing, indicating considerably more catalyst charge than necessary was present). During site visits it was observed that, as a rule of thumb, the systems were typically operated at 10% less NOx removal efficiency than the specified design condition. Conversely, if 90-95% NOx removal control were to be required and enforced, significantly shorter catalyst lifetimes would be expected.

Actual operational control(4) is based on "measuring" the flue gas flow by measuring the fuel flow rate and calculating the resulting gas flow rate that should be produced by burning that amount of fuel, or by measuring the steam flow to the turbine and using that as a "measure" of the amount of fuel being burned, and thus the combustion gas produced. The NOx concentration is also "measured", but the lag time (up to 10-15 minutes) of the measuring instrument means this measurement is not an effective for control purposes except for non load-following operations. It appeared that at several plants(13) the NOx level too was a calculated number. Based upon a calculated flue gas flow rate and NOx concentration, the controller logic specified an ammonia feed flow rate. In some cases(11) the ammonia slip measurement was used as a trim signal to adjust the ammonia feed flow rate so that the slip stayed below 5 ppm.

One of the reasons why ammonia monitoring is not used to provide a control signal is that the ammonia meter often works on the principal of splitting the measurement sample into two flow streams. In one stream the ammonia is converted to nitrogen oxide and the total nitrogen oxide is read by an instrument. In the other stream the nitrogen oxide in the exhaust is read directly. The difference between these two reading is proportional to the ammonia content. This is a difficult measurement to make because both the NOx and the ammonia are present in low concentrations, on the order of ppm, and the measurement is really the difference between two nearly equal numbers. This can routinely lead to significant accuracy problems.

As an example of the difficulty of relying upon the accuracy of the operational instrumentation, the following is cited(12). This incident occurred at a Japanese coal-fired plant equipped with SCR, but the conclusions also could apply to oil and gas-fired plants. The utility had been operating the SCR system for two years. Operations had been routine and uneventful. At the end of a third uneventful year of operation they examined the equipment during the annual inspection period, as had been done during the previous two years. They found extensive erosion of the 1st and part of the 2nd and 3rd sections of a 5 section SCR reactor. Also, there were significant bisulfate deposits on the air preheater. A similar experience was reported by the Germans(8), but it occurred in a pilot plant operation. The important point is not that coal ash eroded the catalyst, but that the monitoring instrumentation had not identified that a significant mal-operation and a corresponding loss of substantial NOx control had occurred.

None of the plants visited during prior visits maintained a spare parts inventory(13) for their SCR systems. However, all of the operating staff had received specific training on operations and maintenance from the SCR system supplier, and the system supplier also supplied engineering staff to directly support the utility staff during the annual SCR system inspection. The utility staff for operations and maintenance (the same people perform both tasks) varied from 6 to 14 per shift. The exact size of the staff appeared to be more a function of the utility historical staffing patterns than a function of the SCR system size.

Maintenance problems have contributed to the Japanese regulatory authorities restricting the use of instruments based upon chemiluminescence principles(13). Even in cases where the regulators have not restricted the use of such instruments, it was found that utilities have replaced them with designs based upon infrared and ultraviolet adsorption principles. Studies and the development of new or more reliable instruments are being actively pursued(18). A typical NOx and ammonia instrumentation maintenance schedule is: daily calibration; bi-weekly inspection and cleaning of the meters; tri-monthly maintenance of meters and recorders; annual overhaul of analyzers and recorders; and replacement of the entire instrumentation system after 6 or 7 years.

The other significant maintenance activity is the actions taken to control or remove soot and ammonium bisulfate deposits. Different utilities use different but related processes. For example, at some plants on-line soot blowing of the air preheater is done three times per day for two hours at a time. Blowing is done from the hot and the cold side of the unit. Two tons per hour of steam are used. This planned schedule was based upon prior Japanese experience with other oil-fired plants that injected ammonia for ash conditioning for hot electrostatic precipitator operations, and was selected for the SCR system "just to be safe". During low power operations, soot blowing often is performed on a continuous basis.

One 700 MW boiler system uses 5,000 tons of wash water per washing. In addition to cleaning the bisulfate material out of the wash water, additional treatment is required to remove the high level of ammonia contamination in the water. The washing cycle includes a period to cool down the equipment, to wash, and then to dry the equipment. This takes 24 to about 40 hours, depending upon the equipment size, and is usually performed during a weekend when the system power demand is low.

In the case of the 700 MW unit sited above, air blowing was originally used as the on-line soot removal method. They changed to steam blowing in order to avoid cooling the hot side and further contributing to the bisulfate problem through the impact of the cooled metal on the bisulfate carrying flue gas. The low temperature side of the air preheater is blown once per shift, the hot side once per day. A 200 psi jet is used, and the blowing is continued for a two hour period. Even with these measures, water washing such as discussed above, is required once every three months.

Other utilities report that they employ water washing of the air preheater at least twice a year. Soot blowing of the air preheater, frequently the catalysts themselves, and other equipment items such as the induced-draft fans occurs weekly and after each startup.

APPLICATION TO U.S. OIL-FIRED BOILERS

Since SCR suppliers in the U.S. have not undertaken pilot or demonstration programs such as was done in Japan and Germany in order to qualify the SCR designs for the specific fuels and operating conditions that are anticipated, the level of risk at a U.S. application is greater than that for a Japanese application. That is, the use of SCR systems could place the boiler and plant at significant risk of operational failure and subsequent plant unavailability if the SCR technology application were to exceed currently proven operating conditions.

To be consistent with the Japanese experience, the NOx level entering the SCR system should not exceed about 150 ppm and the SCR system should not be operated during relatively fast or frequent transients or load changes. It is still possible to design SCR system for operations with greater than 150 ppm NOx at the reactor inlet, but then it can not be claimed that the design has been validated through the Japanese operating experience.

The ammonia injection system should be validated through design analysis and or testing, to assure that it introduces a relatively uniform, fully volatilized ammonia gas which has been diluted in a carrier gas such that the ammonia concentration is less than 10%. An appropriate mixing length to allow the ammonia to mix thoroughly within the flue gas is needed so that a uniform gas steam will enter the SCR reactor.

Ammonia contamination of wash waster and fly ash does not appear to have yet been fully addressed by U.S. regulators. Japanese experience has shown that ammonia contamination of fly ash collected at the electrostatic precipitator can be anticipated. This is a serious problem for the Japanese because often they sell their ash to the cement industry, and the ammonia odor makes it unsalable. In the U.S., contamination of fly ash with ammonia means that normal land-fill disposal of the ash may not be possible because of leaching of the ammonia from the stored ash. If, for example, the ammonia slip were 5 ppm and 90% of that were retained by the ash normally present from oil-firing, then the ammonia content in the fly ash would be about 0.14%. However, ammonia leaching(4) has been found to be a problem if the ammonia content in the fly ash is 0.02% or greater.

Ammonia contamination occurs in the wash water used for removing soot and bisulfates. This causes a water cleanup problem. For example, the water wash at a 700 MW unit uses 5000 tons of water for each wash. Ammonia contamination also occurs in the flue gas desulfurization (FGD) system's waste water. This too adds the requirement for a water treatment step before that waste water can be disposed. It has been suggested(6) that ammonia contamination of the FGD waste water is possibly the most significant adverse effect for SCR operations at U.S. electric power plants.

The SCR system designers and the regulatory community need to recognize the relative uncertainty in the measurement of NOx and ammonia, and the controls and emission permit conditions also should recognize that. The consequence of this is that it may be necessary to reduce the ammonia injection rate, as is typically done in Japan, below the "design" injection rate in order to assure that very low levels of ammonia bypass the SCR reactor. This will be especially important if sulfur-bearing fuels are burned, and it may actually reduce the level of NOx control that is obtained from the SCR system. However, this approach is necessary if the availability of the entire plant is to be maintained at acceptable levels.

In recognition of the uncertainty that will accompany the application of SCR systems to large, oil-fired boilers, extra space for additional SCR catalyst charge should be designed into the SCR system, SCR catalyst test specimens should be placed in the catalyst reactor and periodically examined, and detailed inspections of the SCR system should be planned and conducted at least yearly. If the design basis assumes that soot and ammonia bisulfate deposits will occur, and if specific control and removal systems are designed into the SCR system, then the risk of uncontrolled deposits will be significantly reduced.

Since there is a significant question about instrumentation accuracy and durability, and since the Japanese experience is mostly for base load operation, and since SCR operation is not required during low load, startup, and shutdown, U.S. regulators should also consider similar adjustments in their requirements for SCR operations. In addition, the typical U.S. requirement for a 15 minute averaging time for emission monitoring may not be realistic and a longer averaging times should be considered.

REFERENCES

1. J. Ando. SCR for Existing Oil-Fired Boilers, August 1988.

2. J. Ando Draft. Report, SO_2 and NOx Control Technology Developments in Japan, January 1987.

3. J. Ando. Recent Developments in SO_2 and NOx Abatement Technology for Stationary Sources in Japan, EPA 600/7-85-040, September 1985.

4. J. Ando. NOx Abatement for Stationary Sources in Japan, EPA 600/7-83-027, May 1983.

5. J. Ando. NOx Abatement for Stationary Sources in Japan, EPA 600/7-79-1080, August 1979.

6. E. J. Cichanowicz and G. R. Offen. Applicability of European SCR Experience to U.S. Utilities, EPRI CS-5361, Vol 2, August 1987.

7. W. Ellison and T. A. Ritter. Survey of Japanese Application of Selective Catalytic Reduction Systems, November 1980.

8. W. Goldschmidt. VKR Full-Scale SCR Experiences in Hardcoal Fired Boilers, EPRI CS-5361, Vol 2, August 1987.

9. H. L. Faucett, et al. Technical Assessment of NOx Removal Processes for Utility Application, EPA 600/7-77-127, November 1977.

10. Jones, G.D., "Selective Catalytic Reduction and NOx Control in Japan, A Status Report", EPA 600/7-81-030, January 1981.

11. P. A. Lowe. Report on the Status of Selective Catalytic Reduction NOx Control as Applied to Gas Turbine Electric Power Generation Plants, NUS-4763, December 1985.

12. P. A. Lowe. Utility Operating Experience With Selective Catalytic Reduction of Flue Gas NOx, Proceeding of the 2nd International Conference on Acid Rain, March 1985.

13. P. A. Lowe. Review of Japanese NOx Control Technology Retrofitted to Coal-Fired Boilers, NUS 4465, January 1984.

14. J. D. Mobley. Assessment of NOx Flue Gas Treatment Technology, Proceedings Joint Symposium on Stationary Combustion NOx Control, IERL-RTP-1080, October 1980.

15. L. J. Muzio, et al. Control of Nitrogen Oxides: Assessment of Needs and Options, Technical Support Document, EPRI EA-2048, Vol 5, July 1983.

16. P. Necker. Operating Experiences with SCR DeNOx Plant in Unit 5 of Altbach/Deizisau Power Station, EPRI CS-5361, Vol 2, August 1987.

17. A. V. Slack. Applicability of Japanese NOx Control in The U.S., DOE/MC/15091-1612, February 1980.

18. K. Suyama. The Improvement of NH_3 Injection Control System For a Selective Catalytic NOx Removal System, EPRI CS-5361, Vol 2, August 1987.

19. T. Suzuki. Development of Dry Type Flue Gas Denitrification Equipment for Boilers (Japanese language), IHI Engineering Review, May 1979.

20. Flue Gas De-NOx System Development of Catalyst for Dry Type (Japanese language), Mitsubishi Juko Giho, July 1980.

NOx Control in a Brown Coal-Fired Utility Boiler

John E. Hofmann
Fuel Tech, Inc., Stamford, CT, USA

Joachim von Bergmann
Fuel Tech GmbH, Frankfurt, Germany

Dr. Dieter Bökenbrink
Professor Dr. Klaus Hein
Rheinisch-Westfälisches Elektrizitätswerk, Germany

ABSTRACT

Rheinisch-Westfälisches Elektrizitätswerk (RWE), initiated a number of tests during 1987 of the NOxOUT(R) Process for NOx reduction on a 150 MWe brown coal-fired boiler. The NOxOUT Process uses urea and enhancer chemicals for the reduction of NOx to molecular nitrogen, water vapor and carbon dioxide. The test objectives of up to 50% NOx reduction and NH_3 slip of <5 ppm were met over a range of operating conditions.

In 1988, a commercial NOxOUT system was subsequently installed on a 75 MWe brown coal-fired boiler to comply with a controlled NOx level of 200 mg/Nm^3 (approximately 100 ppm). NOx was first reduced to 300 mg/Nm^3 (approximately 150 ppm) by the use of combustion modifications. Additional NOx reduction down to 180-195 mg/Nm^3 (approximately 90-98 ppm) has been achieved using the NOxOUT Process. NH_3 slip has been controlled to a level of <2 ppm through the combination of enhancer chemicals plus selective injection.

INTRODUCTION

The Federal Republic of Germany is recognized as a world leader for the control of sulfur and nitrogen oxides emitted from stationary combustion sources. Acid rain arising from these pollutants is not only affecting human health but is also considered to be one of the major contributors to the damage of the fauna, in particular to forests, and to historical buildings (1, 2). Current legislation and local agreements between industry and the state authorities require that nitrogen oxides be reduced to a maximum of 200 mg/Nm^3 (approximately 100 ppm) for all boilers in excess of 300 MW_{th} by the end of this decade.

Rheinisch-Westfälisches Elektrizitätswerk A.G. (RWE) has a total generating capacity of more than 20,000 MW and is the largest utility in the Federal Republic of Germany. One of the major fuels of RWE is brown coal which is burned in power stations of about 10,000 MWe installed capacity, with individual units sized up to 600 MWe.

The Rhinish brown coal differs distinctly from other fossil fuels such as bituminous coals or lignites. A high moisture level of 55 - 62% on a raw coal basis, a variable ash content of 2 - 20%, and a low nitrogen concentration of 0.3 - 0.4%, are typical for this fuel.

Consequently brown coal combustion requires specifically designed fuel preparation circuits and boilers which in conjunction with the fuel properties result in specific flue gas characteristics. The flue gas contains about 20% water vapor resulting in maximum flame temperatures below 1200°C and fairly constant NOx concentrations well below 800 mg/Nm^3 (approximately 400 ppm).

It is noteworthy that this fuel is mostly burned in tangentially fired boilers with jet burners in vertically arranged slits in the walls and/or corners of the combustion chamber. Normal operation with one burner slit always out of service at full load and more slits out of service at partial load differs from the firing mode of higher quality coals and results in asymmetric horizontal temperature distributions in the boiler, which has major consequences, as will be discussed later.

In order to comply with the NOx emission requirements, after having completed extensive large scale testing and economic evaluation of the selective catalytic reduction (SCR) technique (3), and also having reached very promising results with combustion modifications (4), RWE decided to retrofit 37 boilers with a total capacity of 9,300 MWe with alterations to the combustion chamber only. However, there were some indications that the final goal of a maximum NOx emission of 200 mg/Nm^3 (approximately 100 ppm) may not be achievable for all boilers and under all operating conditions. Therefore, additional NOx removal principals would be required. This led to large scale tests of various options of injection systems.

One major option for RWE was the NOxOUT Process $^{(R)}$. The NOxOUT Process licensed through Fuel Tech, N.V. is a relatively low cost retrofit NOx control technology. The NOxOUT Process can be installed with a short downtime and is applicable to a very broad range of fuels and boilers. NOx reductions up to 80% are achievable with this technology (5). The NOxOUT Process can be installed along with combustion modifications to achieve even higher levels of reduction. Hence, the NOxOUT Process is applicable as a primary retrofit application and can be applied in conjunction with combustion modifications.

The NOxOUT Process is based upon the chemical reaction between nitrogen oxides and urea.

$$2NO + NH_2CONH_2 + 1/2\ O_2 \text{ ------> } 2N_2 + CO_2 + 2H_2O$$

The reaction takes place at a temperature of about 925 - 1,100°C. Research on the urea-based process was initiated in 1976 under sponsorship of the Electric Power Research Institute (6). Starting with the EPRI inventions (7, 8), Fuel Tech has made a number of contributions to improve the application of the technology (9, 11), including broadening and/or shifting of the optimum temperature for reaction by the use of Fuel Tech proprietary chemical enhancers (10, 12, 13, 14).

Fuel Tech patented enhancers have also been effective in the control of ammonia formation (11). Ammonia (NH_3), is a by-product of the reaction between NOx and urea that can be formed under certain conditions. Ammonia production is generally undesirable because of the possibility of forming sulfates and bisulfates in the presence of sulfur trioxide and in the contamination of ash, affecting ash disposal options. (Bisulfates have been known to cause fouling in the air preheater area.) The sulfur content of RWE coal (0.2% by weight) and the temperatures of the preheater area (<330°C) could provide a reactive environment for the formation of bisulfates if there is ammonia present.

TEST PROCEDURES

The introduction of the NOxOUT Process to brown coal fired boilers was carried out in various steps. The first preliminary tests had to show:

- at least 30 to 50% NOx reduction is possible with NH_3 emissions, or "slip",below 3.8 mg/Nm^3 (approximately 5 ppm)

- the process is flexible enough to accommodate various combinations of burners in operation
- the process could cope with load variations down to partial loads of 60%
- the process is also effective under simulated flue gas conditions which were expected after the envisaged installation of combustion modifications.

These tests were carried out on a 150 MWe boiler (Unit D, RWE Weisweiler power station, figure 1) during the summer of 1987.

Temporary equipment was used for the D boiler tests which consisted of plastic day tanks for chemical storage, a portable pumping skid, mixing headers for combination of NOxOUT-A solution, enhancers and water, rubber hoses, and distribution headers to split the flow between multiple wall injectors at each of three levels of injection. NOxOUT-A is an aqueous solution of urea and proprietary additives.

The first level of injection was into the upper furnace region at 25 meters. The second level was located immediately before the secondary superheater. The third level was located at the top of the backpass after the primary superheater. A number of different injectors were tried and the final arrangement consisted of sixteen external mix injectors at level one (2 per penetration), nine pin jet injectors at level two, and four internal mix injectors at level three. Steam was used for cooling and atomization for injectors at level one. Air was used for cooling and atomization at levels two and three due to a limited availability of steam.

After the successful completion of the preliminary tests a full scale demonstration was conducted at the same power station on a 75 MWe boiler (Unit C2, figure 2) during the summer of 1988. Combustion modifications, installed during the spring of 1988, reduced the NOx emission from about 450 mg/Nm^3 (approximately 225 ppm) to about 275-325 mg/Nm^3 (approximately 140 - 165 ppm) at full load. The major goal of the Unit C2 demonstration was the successful performance of the NOxOUT Process for 4 weeks of continuous operation, during which the NOx emission must not exceed the guaranteed level of 200 mg/Nm^3 (approximately 100 ppm). In addition, the process was required to meet this emission limit while maintaining ammonia emissions below 5 ppm at all operating conditions.

Based on experience from the D boiler, NOxOUT injectors were installed at three levels; at 19 meters immediately above the burners but below the flue gas recycle and overfire air ports, at 25 meters immediately before the secondary superheater, and at 36 meters at the top of the backpass after the primary superheater. There were 12 penetrations at level one, twelve at level two, and four at level three. External mix injectors were used at all levels. Steam was used as the cooling and atomizing fluid for all injectors.

TEST RESULTS - D BOILER

A. Temperature and Composition Profiles

Prior to the commencement of NOxOUT injection, temperatures were measured at each of the three levels of injection. Temperature measurements were made using water cooled suction pyrometers. Analyses for O_2, CO and NOx were carried out at the same time as the temperature measurements. Typical temperature measurements for 100% load were found to be 1021°C (Level 1), 825°C (Level 2), and 580°C (Level 3).

As expected, in the upper furnace region temperatures near the wall tended to be lower than temperatures towards the center of the boiler. However, the overall temperature profiles tended to be fairly uniform. The temperatures at levels 1 and 2 were within the temperature window for enhanced urea chemicals. The temperature at Level 3 however, was too cold for injection of chemicals available at RWE.

Gas composition profiles for NOx, CO and O_2 were recorded at the three levels of injections. The NOx, CO and O_2 concentrations differed at the three levels. NOx values were highest at level 2. Higher NOx concentrations recorded at level 2 were associated with higher O_2 concentrations at this level. The CO levels were found to be significantly higher at level 1 than other levels. The higher concentration of CO at level 1 indicates that complete burnout has not occurred until after this point.

B. NOx Reduction, Level 1 Injection

Results obtained from injection of mixtures of NOxOUT-A and enhancer at level 1 in the D boiler are shown in Figure 3. The Normalized Stoichiometric Ratio (NSR) is defined as the ratio of NH_2 species injected divided by the initial moles of NOx. Thus one mole of urea per mole of NOx represents an NSR of 2.0. The initial NOx level for these series of experiments was approximately 550 mg/Nm^3 (6% O_2). The results show an essentially linear response to increasing amounts of urea injection.

The effect of enhancer is to shift the temperature window for NOx reduction activity to a lower temperature (5). Thus at a specific operating temperature, the addition of enhancer could result in either increased NOx reduction, decreased NOx reduction or no change in NOx reduction. A decrease in NOx reduction implies that the reaction temperature (in this case approximately 1020°C) is such that the operation is on the high side of the reaction temperature window. There is a benefit in operating on the high side of the reaction temperature window in that by-product NH_3 formation is suppressed while NOx reduction is only slightly diminished (11).

The amount of NOx reduction achieved in these experiments implies a urea utilization in the range of 27% with the low enhancer ratio shifting to 20% for the high enhancer ratio (assuming that each urea molecule is theoretically capable of reducing two molecules of NOx). As Figure 3 indicates, the response of utilization to increasing NSR is essentially flat over the range of NSR investigated. Other studies have shown that utilization will tend to decrease with increasing NSR (5).

C. NOx Reduction, Two Level Injection

Urea and enhancer injection was performed simultaneously at levels 1 and 2 to determine if multiple level injection would significantly (A) increase chemical utilization, (B) reduce NH_3 slip, and (C) increase the NOx reduction.

Results from injection of urea and enhancer at level 1 versus levels 1 and 2 at comparable test conditions are contained in Table 1.

Generally, it can be concluded that urea utilization increases when urea is split between two levels at the same overall NSR. These results were achieved despite a slightly higher overall E/U ratio with two level injection. Although it has previously been found that a higher E/U ratio leads to lower NH_3 slip, NH_3 slip was as high with two level injection as with one. It is believed that NH_3 slip from level 2 was the result of chemical impingement on the superheater platens which were within 5 feet of the point of injection at Level 2. Efforts were made to inject the chemicals between the platens, but it was virtually impossible to completely eliminate direct chemical impingement.

D. Enhancer/Urea Ratio, Control of NH3 Slip

The enhancer/urea (E/U) ratio is one of the most significant process variables in the NOxOUT Process. As previously noted, the enhancer/urea ratio can affect the level of NOx reduction but it is particularly important in the control of NH_3 slip. Ammonia (NH_3) is a by-product of the reaction between NOx and urea that can be formed under certain conditions. The amount of NH_3 produced is a function of various process variables and tends to increase with:

- decreasing temperature
- increasing the reagent to NOx mole ratio (increasing NOx reduction)
- decreasing enhancer/urea ratio.

The amount of NH_3 formed tends to increase with increases in NOx reduction and therefore a trade off occurs when NOx reduction has to be forfeited to maintain low NH_3 levels.

Figure 4 shows a comparison of ammonia slip versus NOx reduction at two different E/U ratios. At the higher E/U ratio less ammonia was generated per increment of NOx reduction. The higher E/U ratio enables NOx reduction to be increased from about 30% to about 50% at 5 ppm of NH_3. NOx reduction can be further increased to about 65% with an NH_3 slip of less than 15 ppm.

E. Burners Out-of-Service

During the demonstration, extensive data collection was undertaken to determine if differences in NOxOUT Process performance could be attributed to a specific burner slit that was out-of-service. Temperature measurements were taken, as previously described, prior to injection with different configurations of burner slits in service. Only slight variations in daily average temperatures indicated that there was no significant temperature difference with any specific burner slit out-of-service.

In addition, process results obtained with the four different burner slits out-of-service indicate no significant difference in process performance. The amount of urea required to achieve a given level of NOx reduction and the level of NH_3 slip were essentially unchanged.

F. Low Excess Air and Low Load

Two of the specific objectives of the demonstration were to determine the flexibility of the NOxOUT Process to respond to reduced load and to low excess air (simulated combustion modification).

Temperature profiles and gas composition analyses obtained at Level 1 revealed significant differences for the modified conditions (Table 2).

Low excess air resulted in a higher temperature and a lower NOx content at level 1. Oxygen content was significantly lower and carbon monoxide (CO) was higher. When load was reduced to 60% the temperature and NOx content dropped. Substantial variation in CO content was observed from point to point at level 1 during the experiment with low excess air. These localized concentration variations of CO could be the result of slow burnout of char. Process results obtained with low excess air and low load are shown in Table 3 and compared with data obtained at normal 100% load conditions.

During the experiments at higher NSR, enhancer alone was injected at level 2 to provide an additional level of control over NH_3 slip.

Experiments at low excess air were initially carried out (exp. H) at the same chemical flow rates as had previously been determined to be the optimum for 100% load conditions (exp.G). The NSR increased from 2.4 to 3.0 because of the lower baseline level of NOx and reduction declined from 49% to 45%.

At 60% load conditions (exp. I) the temperature at Level 1 is lower than at 100% load (954°C vs. 1,021°C). At these conditions a three-fold increase in enhancer rate was required to maintain the NH3 slip at 5 ppm. The fact that an NSR of 3.0 is required to achieve comparable NOx reductions for both low load and low excess air conditions is most likely due to the lower initial NOx concentration in the flue gas.

Overall, these data clearly demonstrate that the amount of enhancer required to maintain NH3 slip below a target level depends upon the temperature at the point of injection. The average temperature at level 1 varied over the range of 954 to 1,065°C. Within this temperature range, the amount of enhancer required to meet NH_3 limits increased from 1 part enhancer to 30 parts urea at 1,065°C to 1 part enhancer to 2 parts urea at 954°C.

TEST RESULTS - C2 BOILER

A. Start-up Tests

Prior to the start-up of NOxOUT injection and soon after the C2 boiler returned to stable conditions with the newly installed combustion modifications, Fuel Tech measured baseline temperature, NOx, O_2 and CO. These measurements were carried out in a grid at each level of injection.

Temperature and gas composition data gathered at 80 and 100% load are shown in Table 4.

The overfire air which diverted a part of the combustion air to the ports above 19m had the effect of extending the primary combustion zone. The first injection level was within this extended combustion zone. As a result of these conditions, the values for both NOx and CO were extremely erratic and averages were considered to be meaningless.

Although temperature levels at 19 meters would appear to be conducive to good NOxOUT reagent utilization, the high CO levels existing at level 1 have the impact of shifting the temperature window in which urea is effective (15). Early injection tests at level 1 were not productive for NOx reduction. It was apparent that the "effective" temperature at these high CO conditions was too high for reasonable urea utilization. Further testing was based on injection at the second (25m) level. The third level of injection (36m) was not required because the total amount of NOx reduction required to achieve <200 mg/Nm^3 proved to be only about 35% which could be readily achieved at level 2.

B. Twenty-Five Meter Level Injection

NOx reductions in the range of 40-50% were repeatedly achieved at relatively low NSR values from baseline NOx levels of 275-325 mg/Nm^3. Figure 5 shows the reductions and utilizations observed at varying NSR values. Although the majority of the tests were performed with straight injectors, some comparative tests were performed using angled injectors. NOx reduction and utilization were not found to be sensitive to different types of injectors.

These tests were carried out at an E/U ratio in the range of 0.3 to 0.6. This range was based on results previously determined to be optimum in the D boiler tests. Specific tests to optimize the quantity of enhancer for the C2 boiler remain to be undertaken.

Tests at 80% load with each one of the four separate burner banks out-of-service showed that the process results were independent of the specific burner bank that was out-of-service. Baseline NOx levels at 80% load were typically in the range of 250-275 mg/Nm^3 compared to 275-325 mg/Nm^3 at 100% load. The NSR required to achieve <200 mg/Nm^3 was about 1.5 and reagent utilization is lower than that achieved at 100% load. The reason for this is postulated to be the higher CO concentration at 80% load. As previously noted, CO shifts the temperature window to lower temperatures, and at the upper end of the window this results in decreased reagent utilization.

C. Ammonia Slip

The Unit C2 contract between RWE and Fuel Tech specified that after the initial optimization portion of the demonstration, the "recipe" for achieving the necessary NOx reductions over a range of operating conditions would be turned over to RWE to test its ability to operate continuously for four weeks. Ammonia slip was a very important consideration for RWE. During the four week acceptance period, 64 analyses of ammonia were to be undertaken to determine compliance with the 5 ppm limit. Fuel Tech performed considerable ammonia sampling and computer modelling to gather information on the potential for ammonia formation.

Samples of flue gas were withdrawn from four locations in the flue gas ducts upstream of the air heater. The flue gas temperature at this point is approximately 325°C. The baseline level of NH_3 was determined before the start of injection and was found to be 0.7 ppm. There was no stratification of NH_3 in the flue gas. Following the start of injection at the second level (25 meters) it was found that the overall specification of <5 ppm of NH_3 could be maintained at both 100% and 80% load while also maintaining NOx at <200 mg/Nm^3.

A computer model of the C2 boiler was utilized in an effort to get a better interpretation of the flow and temperature regimes affecting ammonia formation within the boiler at the second level of injection. Figure 6 shows a computer generated temperature profile at 25 meters and the location of the 12 injectors. The model showed that velocity and temperature are influenced by the boiler throat which starts right above the 25 meter level. This throat shifts the swirl in the flue gas which is characteristic of a tangentially fired boiler. This shift combined with the location of the overfire air ports results in cooler areas in the front right and back left corners away from the core of the swirl. This suggested that injection into these cooler regions might be leading to NH_3 slip.

Elimination of five of the twelve injectors at level two combined with an enhancer/urea ratio of about 0.6 led to the extremely low levels of NH_3 slip. A total of 64 individual analyses for NH_3 were carried out over a one month period; 24 at 100% load and 40 at 80% load. The overall average of 1.5 ppm is less than one ppm above baseline. The overall amount of slip is well below the target of 5 ppm.

CONCLUDING REMARKS

The results of the above described projects at the two brown coal fired boilers can be summarized as follows.

- A NOx reduction of 40 to 50% can be achieved with less than 5 ppm of NH_3 slip. Higher NOx reductions are possible depending on the ability to achieve a good distribution of the chemicals and/or on the availability of multiple levels for injection.
- In particular, with a NOx emission of 300 mg/Nm^3 (approximately 150 ppm) or less, which was established by the application of combustion modifications, the intended emission value of less than 200 mg/Nm^3 (approximately 100 ppm) can be reached with an NH_3 slip of well below 5 ppm.
- The use of enhancer is effective in the control of NH_3 slip over various boiler loads especially when load changes result in temperature shifts within the boiler.
- The process is effective at various loads and operating conditions, without having to change injectors.
- Reagent utilization increases with multiple level injection of urea where more than one level is available at appropriate temperatures.
- The use of enhancer permits the chemical utilization to be optimized for a specific reaction temperature.
- The process can be easily retrofitted on an existing boiler with only small disruption to on-going operations.
- RWE's performance objectives for NOx reduction were met by the NOxOUT Process. Further optimization of operating cost can be achieved as the technology evolves. This will be done by optimizing chemical treatment and injection parameters for specific boiler applications.

REFERENCES

1. Mohnen, V.A., "The Challenge of Acid Rain", Scientific American, Vol. 259, No. 2, 30-38, August, 1988.

2. Bruck, R.I., "Decline of Boreal Forest Ecosystems in Central Europe and the Eastern North America - Links to Air Pollution and the Deposition of Nitrogen Compounds", 1987 Joint Symposium on Stationary Combustion NOx Control, March 23-26, 1987, New Orleans, LA

3. König, J., Derichs, W., Hein, K., "Untersuchungen zum Einsatz der SCR-Technik hinter Braunkohlefeuerungen", Sonderheft der Zeitschriften BWK, TÜ und Umwelt im VDI-Verlag (1988), Heft 10

4. Hein, K., "The Application of Combustion Modifications for NOx Reduction to Low-Rank Coal-Fired Boilers", 1989 Joint Symposium of Stationary Combustion NOx Control, March 6-9, 1989, San Francisco, CA.

5. Epperly, W.R., Broderick, R.G., and Peter-Hoblyn, J.D., "Control of Nitrogen Oxide Emissions from Stationary Sources", American Power Conference, April 20, 1988, Chicago, IL.

6. Muzio, L.J., and Arand, J.K., "Homogeneous Gas Phase Decomposition of Oxides of Nitrogen", EPRI Report No. FP-253, 1976.

7. Arand, J.K., and Muzio, L.J., "Urea Reduction of NOx in Combustion Effluents", U.S. Patent #4,208,386 (1980).

8. Arand, J.K. and Muzio, L.J., "Urea Reduction of NOx in Fuel-Rich Combustion Effluents", U.S. Patent #4,325,924 (1982).

9. Epperly, W.R., Peter-Hoblyn, J.D., Shulof, G.F. and Sullivan, J.C., "Multi-Stage Process for Reducing the Concentration of Pollutants in an Effluent", U.S. Patent #4,777,024 (1988).

10. Epperly, W.R., and Sullivan, J.C., "Process for the Reduction of Nitrogen Oxides in an Effluent", U.S. Patent #4,770,863 (1988)

11. Epperly, W.R., O'Leary, J.H., and Sullivan, J.C., "Process for Nitrogen Oxides Reduction and Minimization of the Production of Other Pollutants", U.S. Patent #4,780,289 (1988).

12. Epperly, W.R. and Sullivan, J.C., "Process for the Reduction of Nitrogen Oxides in an Effluent", U.S. Patent #4,803,059 (1989).

13. Bowers, W.E., "Reduction of Nitrogen-Based Pollutants Through the Use of Urea Solutions Containing Oxygenated Hydrocarbon Solvents", U.S. Patent #4,719,092 (1988).

14. Bowers, W.E., "Reduction of Nitrogen - and Carbon-Based Pollutants", U.S. Patent #4,751,065 (1988).

15. Caton, J.A. and Siebers, D.L., "Comparison of Nitric Oxide Removal by Cyanuric Acid and by Ammonia", Paper No. 88-67, Western States Section/The Combustion Institute Fall Technical Meeting, Dana Point, CA, October, 1988.

TABLE 1
SINGLE VS. TWO LEVEL INJECTION

Experiment	A	B	C	D	E	F
No. of Levels	1	2	1	2	1	2
NSR (1)	1.2	1.0	2.7	2.6	3.0	3.3
E/U (2)	0.1	0.15	0.2	0.56	0.03	0.2
% Reduction	31.4	44.6	51.0	64.0	44.0	50.5
%Utilization	26.0	45.0	19.0	24.0	14.5	15.5
NH_3, ppm	13.0	14.0	20.5	—	—	12.9

(1) NSR=ratio of NHi moles injected divided by the initial moles of NOx
(2) Weight ratio of Enhancer to Urea

TABLE 2
EFFECT OF BOOS ON TEMPERATURE AND GAS COMPOSITION

Operation	Conventional Excess Air 100% Load	Low Excess Air 100% Load	Conventional Excess Air 60% Load
Level 1			
Avg. Temp, °C	1,008	1,065	954
Avg. NOx mg/Nm^3 (1)	460	321	362
Avg. CO, ppm	47	700	38
Avg. O_2, vol. %	5.2	2.2	5.7
Level 2			
Avg. Temp, °C	811	878	804
Avg. NOx mg/Nm^3 (1)	513	328	347
Avg. CO, ppm	11	330	0
Avg. O_2, vol. %	6.3	3.1	5.5
Stack			
NOx, mg/Nm^3 (1)	584	403	427
CO, ppm	6	3	0
O_2, vol. %	7.1	4.5	7.6

(1) Corrected to 6% O_2.

TABLE 3
EFFECT OF MODIFIED OPERATION ON NOxOUT PROCESS

Operation	Conventional Excess Air 100% Load	Low Excess Air 100% Load	Conventional Excess Air 60% Load
Experiment	G	H	I
Baseline NOx	580	403	427
Level 1			
NSR	2.4	3.0	3.0
E/U	0.14	0.03	0.5
Level 2			
EWR (1)	0.33	0.13	0.42
% Reduction	49	45	48
% Utlization	20	16	18
NH_3, ppm	4.5	3.5	5.0

(1) Weight ratio of enhancer to baseline NOx (as NO_2).

TABLE 4
C2 BOILER – TEMPERATURE AND GAS COMPOSITON

Load	100%		80%	
Level	1(19 m)	2(25 m)	1(19 m)	2(25 m)
Temperature, °C	1040	995	992	980
NOx, mg/Nm^3	250–400	250–350	150–400	150–400
CO, ppm	500–10000	70–3000	10000–30000	250–10000
O_2, %	3.2	4.1	1.2	4.2

Fig.1. R.W.E. D BOILER

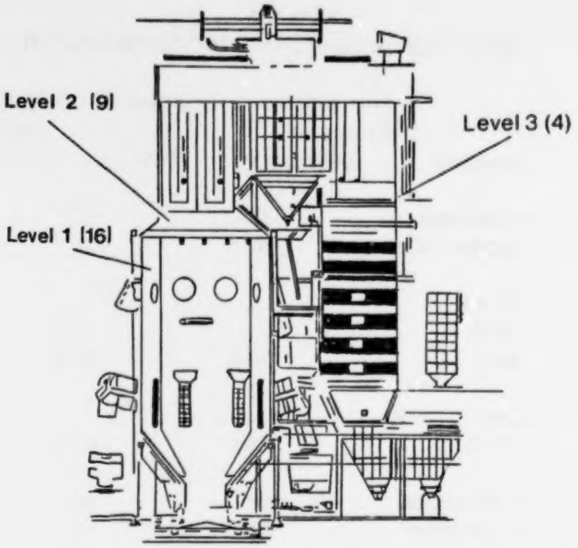


Fig. 2. R.W.E. C2 BOILER

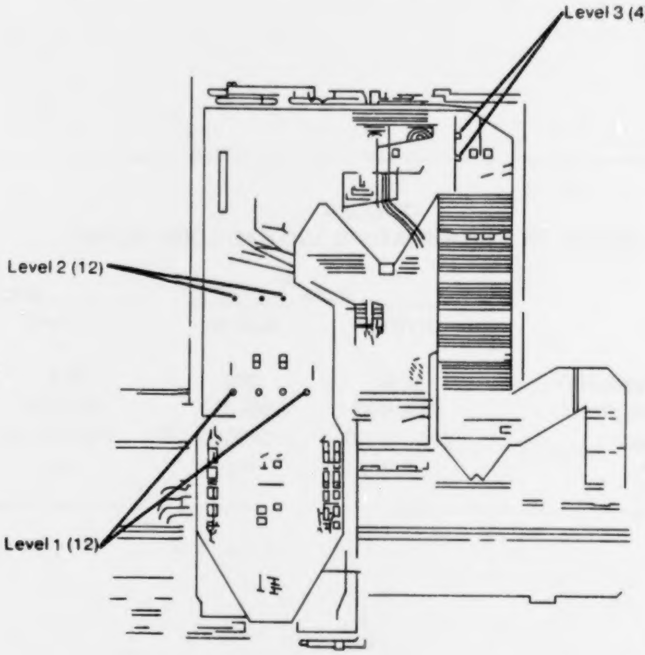


Fig. 3. NOx REDUCTION AND UTILIZATION vs. NSR
R.W.E. UNIT D

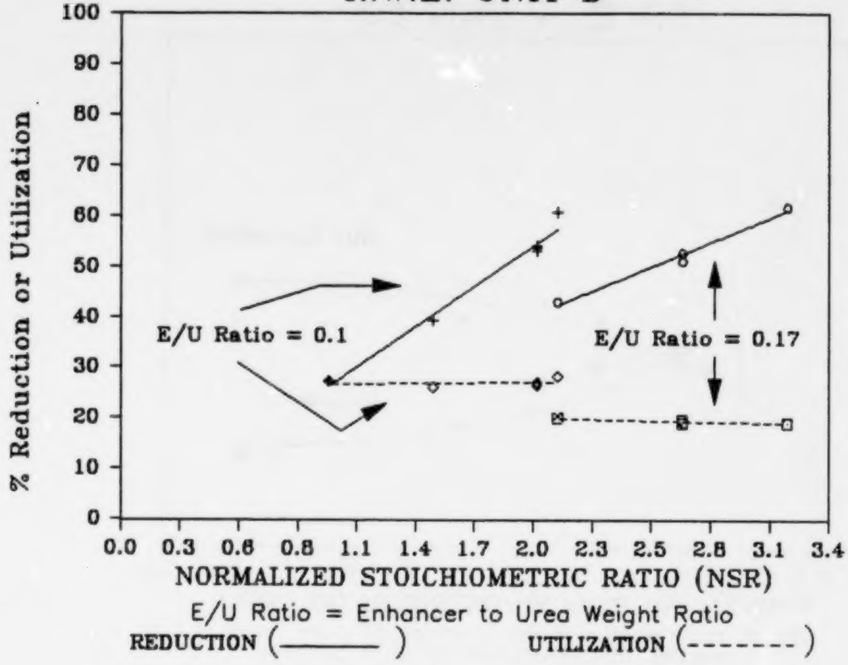


Fig. 4. AMMONIA vs. PERCENT NOx REDUCTION
R.W.E. – UNIT D

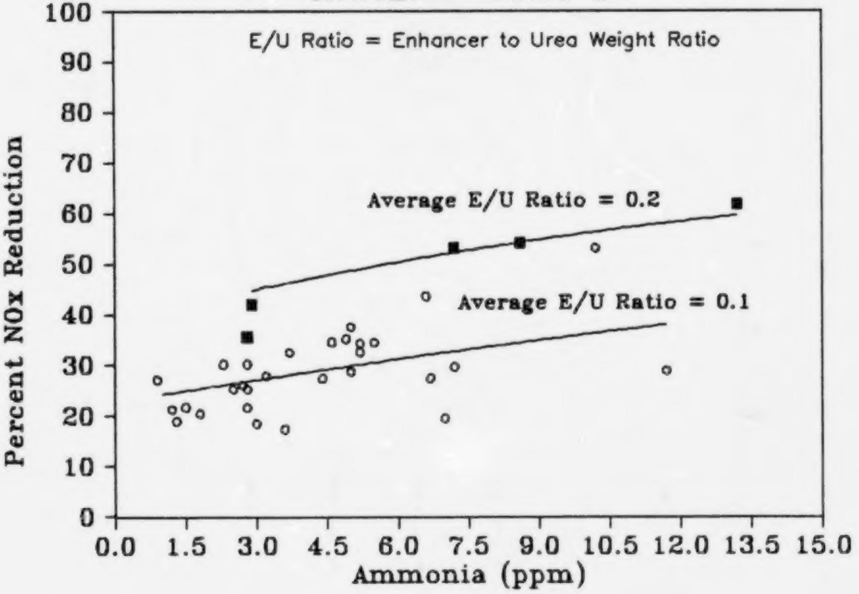
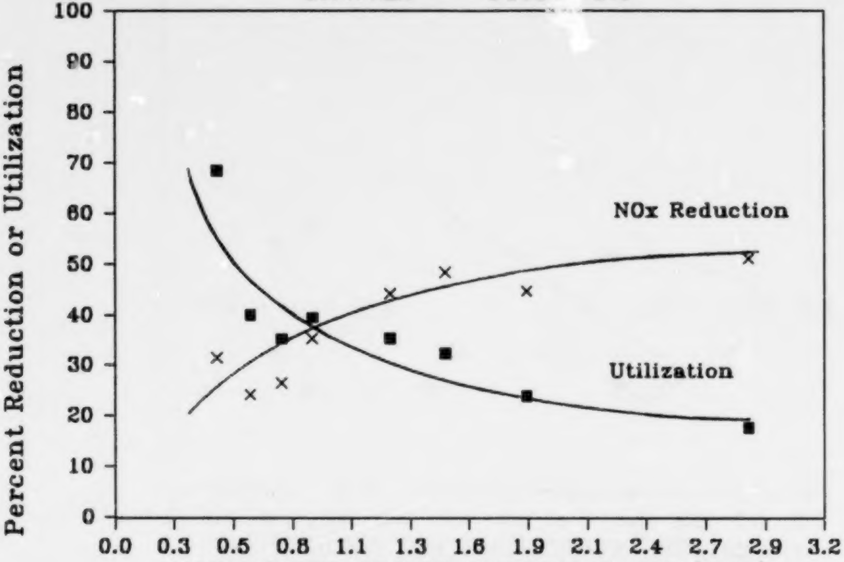
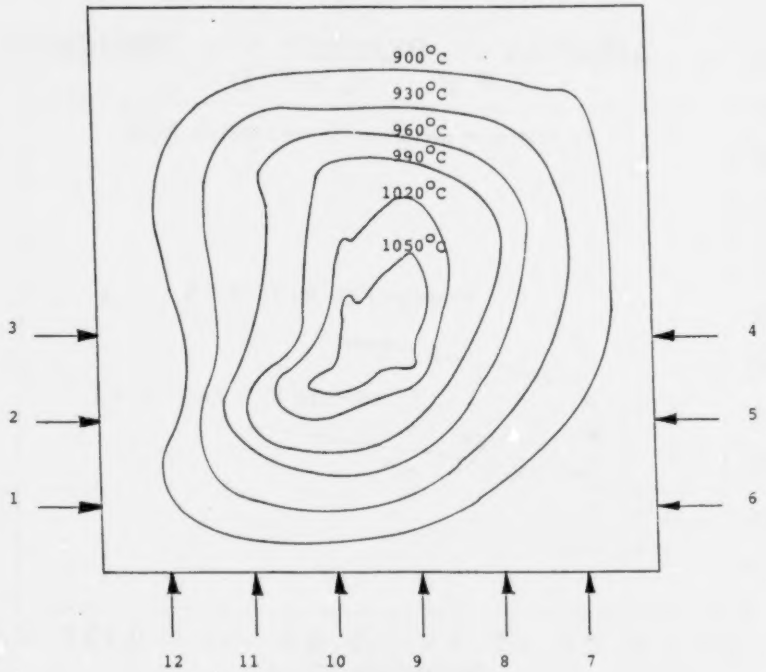


Fig. 5. NOx REDUCTION AND UTILIZATION vs. NSR
R.W.E. – UNIT C2



NSR = molar ratio of the amount of urea used relative to the amount of NOx present

Fig. 6. FURNACE MODELLING – TEMPERATURE PROFILE
R.W.E. C2 BOILER – 25m LEVEL



Session 7B

FUNDAMENTAL COMBUSTION RESEARCH

Chairman: W. Linak, EPA

FORMATION OF NITROUS OXIDE FROM NO AND SO2 DURING SOLID FUEL COMBUSTION

G. G. de Soete
Institut Français du Pétrole
1-4 Avenue de Bois-Préau
92506 Rueil-Malmaison Cedex
France

ABSTRACT

In recent months the formation of nitrous oxide as a product of reactions between nitric oxide and sulfur dioxide or sulfite, has been highlighted in relation to "artificial" N2O formation during storage of flue gas samples. Closer examination shows, these reactions to bear a rather general character. The value of their overall rate constant as well as its temperature dependence also suggest, that they may occur under typical heterogeneous combustion temperatures and residence times, whenever sulfur compounds are present in the fuel, or whenever such sulfur species are formed form e.g. lime stone, added for the sake of sulfur capture. The present paper focusses on the formation of nitrous oxide due to the reactions of NO with reduction products (CaSOR) of sulfates, in the temperature range of 1000 to 1400 Kelvin. The reduction of sulfate in this range mainly occurs on bound carbon atoms of the solid fuel. In the case of a coal char, the N2O formation from NO + CaSOR interferes with N2O formation from char bound nitrogen. In order to avoid this interferes with N2O formation from char bound nitrogen. In order to avoid this interference, pure graphite has been utilized as a fuel. Moreover, proper determination of the rate of the reaction 2 NO + CaSOR $\longrightarrow$ N2O + CaSO4, requires the knowledge of (1) the reduction rates of the sulfate by bound carbon and by carbon monoxide and (2) the concomitant heterogeneous reduction rates of N2O on bound carbon atoms; these rates therefore have been determined separately in the same experimental apparatus. The rate constant of reaction 12, as determined in the 1100-1400 K range, shows to be identical (within the limits of precision) with the one formerly obtained under ambient temperature conditions. Further study is in progress to check (1) the role of specific sulfur compounds (sulfites, sulfides, SO2) and (2) the influence of oxidizing conditions on this type of N2O formation.

INTRODUCTION

Nitrous oxide is released as a reduction product of NO or NO2 during the reactions of the latter with SO2, either in the gas phase or in ionic solutions ([1,2]). AT ambient temperature, these reactions are relatively slow, however fast enough to jeopardize seriously nitrous oxide analyses made on flue gas samples, when stored in containers for some hours.

In the temperature range of 0 to 70 °C, an approximate value of the overall N2O formation rate has been obtained ([2]), which, for example in the case of gas phase formation of N2O from NO and SO2 in the absence of oxygen, may be expressed as :

$$V_{N20} \simeq 5\ 10^{-1} \exp(-1500 \text{ to } 2000/T)\ P_{NO}\ (ng_{SO2}/cm^3) \qquad (ng/h)$$

Boldly extrapolating this rate towards typical coal combustion conditions of temperature, concentrations and residence times, it is suggested that reactions of that kind might play a role in the N20 emissions from solid fuel combustors (especially of the fluidized bed type), where they are likely to interfere with other NO2 producing, homogeneous and heterogeneous mechanismes.

Scope of this study is to check the possible N20 formation due to heterogeneous reactions of NO with sulfate decomposition and reduction products (such like sulfites, sulfides, SO2, H2S). Some of these reduction products may be naturally present in the coal or char; others will form from sulfates obtained during sulfur capture techniques. The study aiming at the establishment of overall rate constants, it is important to avoid any interference with N20 formation from fuel bound nitrogen atoms occuring during combustion, and to correct the global N20 yields for the, unavoidable, heterogeneous reduction of the latter on fuel bound carbon atoms. This is done by utilizing pure graphite as a fuel and by determining separately, on the same apparatus, the heterogeneous reduction rates of N20 on graphitic carbon. Further is it required to know the overall reduction rate of the sufate, i.e. the production rate of sulfate reduction products due to the presence of reducing agents such like bound carbon or CO; these reduction rates also have been determined separately on the same apparatus, in the absence of NO, and counterchecked in the presence of NO.

EXPERIMENTAL METHOD

A fixed bed method has been utilized. The reactor is a quartz tube of 11 mm i.d., placed vertically in an electrically heated oven. The solid phase, constituting a bed of 8 mm height, is a mechanical mixture of high purity graphite (99.999 % purity, 25 microns size) and CaSO4 (of 5 to 10 microns particle size); this solid phase, situated in the center of the electrical oven, supported by a sintered quartz plate, is further diluted by non porous, 100 microns sized quartz beads working as a thermal buffer. The gas phase, flowing downward through the bed, is either NO + argon, or N20+argon (for the study of heterogeneous reduction of nitrous oxide en graphitic bound carbon; for these trials there is no sulfate mixed with the graphite), or pure argon (for the study of CaSO4 reduction by graphite), or CO+argon (for the determination of CaSO4 reduction rate by carbon monoxide, in the absence of graphite).

A Nickelchrome/Nickel thermocouple, placed in the center of the bed, monitors the instantaneous temperature of it. Outlet gases are continuously analysed for CO, CO2, NO and O2 (recording frequency = 0.5 Hertz), and discontinuously for N20 (on-line gas chromatograph equipped with a back-flushed porapak column in series with a molecular sieve column and an EC detector; carrier gas : 5% methane in argon; detection level : less than 0.02 ppm N2O; sampling and analysis every 4 minutes). All analyser and temperature outputs are recorded and treated by a microcomputer. The reactor temperature is either kept constant or increased progressively using a dT/dt value of about 6 degree/minute, which is slow enough to ensure adsorption desorption equilibrium.

EXPERIMENTAL OBSERVATIONS

We succesively consider (1) the phenomenon of the reduction of sulphate into its reduction products ($CaSO_R$) by either CO or bound carbon, and (2) the reduction of NO into N2O on these sulfate reduction products.

Reduction of CaSO4 by Carbon Monoxide and Bound Carbon

Reduction of Sulfate by CO. Upon heating sulfate in the absence of any reducing agent, it decomposes into the oxide and SO2 :

$$\mathrm{CaSO4} \xrightarrow{1} \mathrm{CaO} + \mathrm{SO2} + 1/2\ \mathrm{O2}$$

For calcium sulfate, this decomposition is negligible below 1400 K, and therefore the overall reaction I schould not be taken into account in the present study.

It is known form the literature (3), that alkaline earth sulfites, such as CaSO3, also thermally decompose in the oxyde and SO2, whereas alkali sulfites undergo auto-oxireduction, according to the overall reactions :

$$\mathrm{CaSO3} \xrightarrow{2} \mathrm{CaO} + \mathrm{SO2}$$
$$4\ \mathrm{Na2SO3} \xrightarrow{3} 3\ \mathrm{NaSO4} + \mathrm{Na2S}$$

In the presence of CO as a reductant, calciumsulfate is reduced already at 1000 K, under formation of CO2 and a, provisoriously not defined reduction product ($CaSO_R$)

$$\mathrm{CaSO4} + \mathrm{CO} \xrightarrow{11} \mathrm{CaSO}_R + \mathrm{CO2}$$

where $CaSO_R$ designates a whatsoever sulfate reduction product stripped by one oxygen atom with respect to sulfate; its concentration, ($CaSO_R$) is expressed "per oxygen atom stripped" and therefore is given by the sum of (4-n) times the concentration of each particular $CaSO_n$ species, e.g. :

$$(\mathrm{CaSO}_R) = 0\ (\mathrm{CaSO4}) + (\mathrm{CaSO3}) + 2\ (\mathrm{CaSO2}) + 4\ (\mathrm{CaS}) \qquad (1)$$

Figure 1 shows an example of reduction of CaSO4 by CO; it clearly indicates the oxygen/carbon balance of reaction 11 :

$$CaSO_R \text{ formed} = CO_{in} - CO_{out} = CO2_{out} \qquad (2)$$

Reduction of Sulfate by Graphite. The reduction of CaSO4 by graphite bound carbon yields CaS and mainly CO2. some smaller quantities of CO being observed also. Designating by "a" the ratio of CO/CO2 in the outlet gases, one may write the overall reaction as :

$$(2+a)\ CaSO4 + (1+a)\ (-C) \xrightarrow{10} (2+a)\ CaSO_R + CO2 + a\ CO$$

Figure 2 shows typical CO/T and CO2/T profiles measured during thermal treatment under argon flow of an anhydrous CaSO4/graphite mixture. At temperatures between 770 and 940 K, a first phase of partial sulfate reduction occurs, as shown by the F_0/T curve. F_0 designates the fraction of oxygen atoms removed from the sulfate molecule. During this first, L(ow) T(emperature) phase of reduction, only CO2 appears as a carbon oxidation product. At temperatures higher than 1130 K, a second, H(igher) T(emperature) phase of reduction starts, releasing both CO and CO2. In the trial presented on figure 2, the final temperature has been maintained for about one more hour, until CO and CO2 outlet concentrations had dropped to zero. At that final instant, the fraction of carbon consumed (F_C) had reached a value of about 0.38 and the fraction F_0 a value of about 0.43. The reduction of calcium sulfate by graphitic bound carbon thus presents at least two successive and separate steps : a LT step, yielding only CO2, and a HT step, starting beyond 1130 K, yielding mainly CO2 and some CO and removing a much larger fraction of oxygen atoms form the sulfate.

In neither of these two reduction steps does the reeaction involve the total mass of sulfate present. This is mainly due to the fact that the mechanical mixture of graphite and sulfate particles does not provide an ideal reaction interface.

Reduction of NO into N2O by Sulfate Reduction Products

As an example, figure 3 shows the evolution of NO, N2O, CO, CO2, F_C and F_0 with temperature in a batch trial where NO is fed over a calcium sulfate/graphite mixture. As far as the nitrogen species are concerned, one observes the following :

(a) At temperatures below about 1230 K, a slow decrease of NO and N2O occurs, which is accounted for by the heterogeneous reduction of these two species on bound carbon atoms, as may be seen from the comparison of the corresponding NO/T and N2O/T profiles obtained on pure graphite (i.e. in the absence of sulfate) with identical NO/Ar or N2O/Ar mixtures (curves B).

The reduction of NO on graphite mainly produces N2 and CO, which may be accounted for by the reactions (4) :

$$NO + 2\ (-C) \xrightarrow{4} (-CO) + (-C\cdots N)$$

$$2(-C...N) \xrightarrow{5} N2 + 2(-C)$$

$$(-CO) \xrightarrow{6} CO + \text{free carbon site}$$

and corresponds to the experimental overall mass balance (^{5}) :

$$NO_{in} - NO_{out} = CO_{out} \qquad (3)$$

whereas, in the reduction of N2O on graphite, the main carbon oxidation product is CO2, according to the reactions (^{5}) :

$$N2O + (-C) \xrightarrow{7} N2 + (-CO)$$

$$N2O + (-CO) \xrightarrow{8} N2 + CO2 + \text{free carbon site}$$

$$\text{or : } 2(-CO) \xrightarrow{9} CO2 + (-C) + \text{free carbon site}$$

corresponding to the mass balance :

$$N2O_{in} - N2O_{out} = 2\ CO2_{out} \qquad (4)$$

(b) However, at temperatures beyond 1240 K, the NO/T and N2O/T evolution profiles, measured in the presence of sulfate (curves A on figure 3), show a quite different shape than in the case of pure graphite (curves B).

The fast decrease of nitric oxide apparently cannot be accounted for by its sole heterogeneous reduction on bound carbon. The N2O outlet concentration starts increasing (instead of continuing to decrease as in the case where no sulfate is present), then passes through a maximum before decreasing again, suggesting that, in the given temperature range, it is the result of two competing reactions : (1) a formation reaction, in which sulfate reduction products thus appear to play an important role and which we shall assume to correspond to the overall reaction :

$$2\ NO + CaSO_R \xrightarrow{12} N2O + CaSO4$$

and (2) a destruction reaction, most likely the already mentioned heterogeneous reduction on bound carbon (reaction 7).

DETERMINATION OF THE RATE CONSTANTS

The rate constants k_{10}, k_{11} and k_{12} have been determined from the experimental values of the time variations of N2O and $CaSO_R$, respectively measured as :

$$\frac{dN2O}{dt} = v_{N2O} = 2M_N D(X_{N2O,out} - X_{N2O,in})/v_M \qquad (g_{N2O} \text{ as } N/s) \qquad (5)$$

$$\frac{dCaSOR}{dt} = v_{CaOS_R} = \left[(m_{Osulf})_t - (m_{Osulf})_{t-\Delta t}\right]/\Delta t \qquad (g_{CaSO_R} \text{ as } O/s) \qquad (6)$$

where X is mole fraction, M_N the atomic mass of N, v_M molar volume at TPN and D the gas flow rate at TPN; m_{Osulf} is the mass of oxygen removed from the sulfate, obtained as :

$$m_{Osulf} = M_O D \int_0^t (2\Delta X_{CO2} + \Delta X_{CO} - \Delta X_{NO} - \Delta X_{N2O}) dt / v_M \qquad (7)$$

where M_O is the atomic mass of oxygen; ΔX_j stands for $X_{j,in} - X_{j,out}$. The fraction of oxygen atoms removed from the sulfate (F_O) is related to m_{Osulf} by the expression :

$$F_O = m_{Osulf}\, M_{sulf} / 4 M_O (m_{sulf})_i \qquad (8)$$

where M_{sulf} is the molar mass of CaSO4 and $(m_{sulf})_i$ the initial mass of sulfate present in the reactor.

Determination of Constant k_{12}

When NO is fed over a mixture of graphite and CaSO4, one has :

$$V_{N2O} = V_{12} - V_7 - V_8 = V_{12} - V'_7 \quad (\text{with } V'_7 \equiv V_7 + V_8) \qquad (9)$$

One therefore has to determine the rate V'_7 prior to abtain V_{12} and k_{12}. Determination of the heterogeneous N2O reduction rate on bound carbon is made in the same apparatus, feeding N2O/argon mixtures over graphite. Reaction rate V'_7 is found to be first order in graphite mass and in partial N2O pressure (^{5}) :

$$V'_7 = k'_7\, m_C\, \overline{P_{N2O}} \qquad (g_{N2O \text{ as } N}/s) \qquad (10)$$

where m_C is the instantaneous value of the mass of carbon present, equal to its initial mass (m_{Ci}) when multiplied by $(1-F_C)$:

$$F_C = \int_0^t (X_{CO,out} + X_{CO2,out}) dt\, D\, M_C / m_{Ci} v_M \qquad (11)$$

and $\overline{P_{N2O}}$ the mean value of the partial N2O pressure between reactor inlet and outlet :

$$\overline{P_{N2O}} = P(X_{N2O,in} + X_{N2O,out})/2 \qquad (12)$$

The rate constant k'_7 has been determined by integral treatment of the reactor (^{5})

$$k'_7 = 2 M_N D \ln(X_{N2O,in}/X_{N2O,out})/P\, v_M + 8.0 \exp(-16400/T) \qquad (g_N/g_C\, sP_a) \qquad (13)$$

V_{12} may now be determined from eq(9) as the sum $(V_{N2O} + V'_7)$, and is found to be approximately first order in the partial NO pressure and in $CaSO_R$. It therefore may be expressed as :

$$V_{12} = k_{12}\, m_{SR}\, \overline{P_{NO}} \qquad (g_{N2O \text{ as } N}/s) \qquad (14)$$

with :

$$\overline{P_{NO}} = P\,(X_{NO,in} + X_{NO,out})/2 \qquad (15)$$

P indicating total pressure. m_{SR} is the instantaneous value of the mass of sulfate (expressed as mass of S) reduced into $CaSO_R$:

$$m_{SR} = m_{Osulf}\ M_S/M_O = 4\ F_O\ M_S(m_{sulf})_i/M_{sulf} \qquad (16)$$

The value of k_{12}, as obtained with CaSO4, is given by (see figure 4) :

$$k_{12} = 5.0\ 10^{-7}\ \exp(-2000(+\ 500)/T) \qquad (g_{N2O}\ \text{as}\ N/g_S s\ Pa) \qquad (17)$$

This constant should be compared with that obtained at room temperature for the N2O formation from NO and SO2 (^{2}) ; when expressed in the same units as eq. (17), the latter may be written as :

$$k_{12} = 1\ \text{to}\ 4.8\ 10^{-7}\ \exp(-1500\ \text{to}\ -2000/T) \qquad (18)$$

The surprising similarity of these two overall rate constants as determined in the 1240-1350 Kelvin range and in the 273-340 Kelvin range, seems to indicate that an analogous mechanism of N2O formation is at work in both cases (see figure 5).

Determination of Rate Constant k_{11}

Feeding CO over CaSO4, the reduction rate of the latter is equal to the experimental value of V_{CaSR}, which in this particular case is equal to the CO consumption rate :

$$V_{11} = V_{CaSOR} = M_O D(X_{CO,in} - X_{CO,out})/v_M \qquad (g_O/s) \qquad (19)$$

Rate V_{11} is found experimentally to be first order in partial CO pressure and in the mass of oxygen "available for reaction" in the sulfate. By "available for reaction" one should understand that fraction of oxygen which actually can be stripped from the sulfate, owing to the fact that, due to the non ideal solid/gas interface, not all the oxygen atoms are able to react. This "available fraction" will be designated by F_{Oav}, which is the final value of F_O obtained at the end of a batch trial, when the $CO2_{out}$ concentration has dropped to zero again and the CO_{out} concentration has become again equal to CO_{in} (see figure 1). Rate constant k_{11} may thus be determined from the expression :

$$V_{11} = k_{11}\ m_{Oav}\overline{P_{CO}} \qquad (20)$$

where $\overline{P_{CO}}$ is the mean partial pressure of CO in the reactor :

$$\overline{P_{CO}} = P(X_{CO,in} + X_{CO,out})/2 \qquad (21)$$

The value of m_{Oav} may be calculated as a function of F_O :

$$m_{Oav} = 4\ M_O(m_{sulf})_i(F_{Oav} - \overline{F_O})/M_{sulf} \qquad (22)$$

where :

$$\overline{F_O} = (F_{O,at\ t} + F_{O,at\ t+\Delta t})/2 \qquad (23)$$

According to eqs (19) and (20), k_{11} is thus obtained in the units $Pa^{-1}s^{-1}$. Values of k_{11} determined in that way as a function of temperature are given on figure 4. Its expression corresponds to :

$$k_{11} = 2.8\ 10^{6} \exp(-33500/T) \qquad (Pa^{-1}s^{-1}) \qquad (24)$$

Determination of rate constant k_{10}

Rate constant k_{10} has been determined both in the presence and in the absence of NO, both methods yielding the same value.

In the Absence of NO. In the LT reduction phase, there is no CO production; V_{10} therefore is directly obtained as :

$$V_{10} = V_{CaSOR} = 2\ M_{O}D(X_{CO2,out})/v_{M} \qquad (g_{O}/s) \qquad (25)$$

In a first approximation V_{10} shows to be first order with respect to both mass of graphite and mass of sulfate; it therefore may be written as :

$$V_{10} = k_{10}m_{Oav}m_{C} \qquad (g_{O}/s) \qquad (26)$$

For LT reduction of Calcium sulfate, the following value of k_{10} has been determined

$$k_{10,LT} = 4.7\ 10^{6} \exp(-18200/T) \qquad (g_{C}{}^{-1}S^{-1}) \qquad (27)$$

During the HT reduction phase, some CO is produced; therefore V_{10} is to be determined as :

$$V_{10} = V_{CaSO_R} - V_{11} = k_{10}m_{Oav}m_{C} \qquad (g_{O}/s) \qquad (28)$$

One obtains for k_{10} in the HT reduction phase :

$$k_{10,HT} = 5.4\ 10^{11} \exp(-40\ 000/T) \qquad (g_{C}{}^{-1}s^{-1}) \qquad (29)$$

Values of $k_{10,HT}$ are compared to those of k_{11} as a function of temperature on figure 4, $k_{10,HT}$ being given by curve A .

In the Presence of NO. For the determination of k_{10} in the presence of NO, the experimental value of V_{CaSO_R} should be corrected for the existence of V_{12} and V_{11} :

$$V_{10} = V_{CaSO_R} + M_{O}\ V_{12}/2M_{N} - V_{11} \qquad (g_{O}/s) \qquad (30)$$

The value determined for $k_{10,HT}$ is almost identical to that obtained in the absence of NO (see figure 4, curve B).

Comparison of eqs (27) and (29) suggests that, at LT one is dealing with a different reduction type than at HT; for example : reduction of sulfate into sulfite at LT, and reduction of sulfate into sulfide at HT. More work is in progress to elucidate this question. using sulfites and sulfides mixed with graphite.

CONCLUSIONS

1. Experimental evidence has been obtained of the existence of nitrous oxide formation from NO and sulfur compounds under combustion temperature conditions. A striking parallelism has been found with analogous reactions, recently studied at room temperature, showing an almost identical rate constant. The similarity of the subjacent mechanism is obvious (see figure 6) :
   (a) In the ambient temperature range, and more specially in the ionic state, sulfur compounds may be either oxidized or reduced by NO. the latter playing its double oxidant/reductant role (figure 6, B). Oxidizing sulfite ions or SO2 into sulfates or SO3, nitric oxide is reduced into N2O. and NO2 is reduced into NO. Reducing in turn the sulfate ion, nitric oxide oxidizes into NO2, thus completing the cyclic mechanism ([2]).
   (b) In the combustion temperature ranges, contact times of NO with sulfate being very short. compared to usual room temperature situation, the sulfate reduction step is more efficiently played by bound carbon atoms or CO (figure 6, A). In the typical case of calcium sulfate this reduction step requires temperatures beyond 1200 K. The possibility of this reduction under oxidizing conditions is now been checked (in progress).
2. A more practical question is the importance of N2O formation by this way. as compared to other N2O production mechanisms at work during solid fuel combustion, e.g. N2O formation from bound nitrogen atoms. Figure 7 shows a comparison. at different temperatures and concentrations of sulfur (m_{SR}). N2O and oxygen, between the overall reaction rates of N2O formation, either from NO+ sulfur species (V_{12}) or from bound nitrogen (V_N) : it is clear from these data. that V_{12}/V_N will become larger than one for either sufficiently high reduced sulfur compound concentrations, or sufficiently low oxygen contents, or at sufficiently low temperatures. This temperature condition situates reaction 12 as a good candidate for N2O formation under fluisized bed conditions, the more since other sulfates (like alkali sulfates) may be reduced at lower temperature than calcium sulfate.

ACKNOWLEDGMENTS

The author wishes to thank Joseph McSorley and William Linak, from the US E.P.A., and Jost Wendt, from the University of Arizona, for their encouragement and continuous interest in the present research work.

REFERENCES

1. L.J., Muzio et alii, "Potential errors in grab sample measurements of N2O from combustion sources", 1988 Fall Meeting of the Western States Section of the Combustion Institute, Dana Point, Ca, October 17-18, 1988, paper n° 88-70.

2. G. G., de Soete, "Parametric study of N2O formation from sulfur oxides and nitric oxide during storage of flue gas samples", Report IFP N° 36 732, December 1988. (available on request).

3. J., Verhulst, J. C., Jungers, and A., Bruylants, "Algemene Scheikunde, Part 1 : Anorganische Chemie", Desoer Edit. Liège, 1953.

4. G. G., de Soete, EPA Project Decade Monograph on Coal Combustion, Chapter 8, "Reduction of nitric oxyde by solid particles" (to be published).

5. G. G., de Soete, "Heterogeneous NO and N2O formation from bound nitrogen during char combustion", Joint Meeting of the British and French Sections of the Combustion Institute, April 18-21 1989, Rouen, France.

   Idem, "Formation hétérogène de protoxyde d'azote à partir de l'azote constitutif de combustibles solides", Report IFP, N° 36 752, March 1989. (available on request).

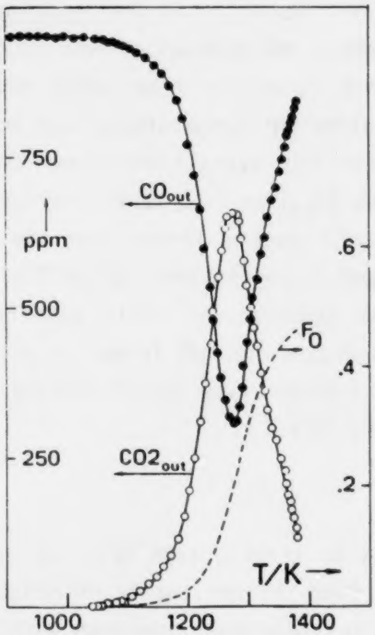


Figure 1. Reduction of CaSO4 by CO.
954 ppm CO in argon on 500 mg CaSO4

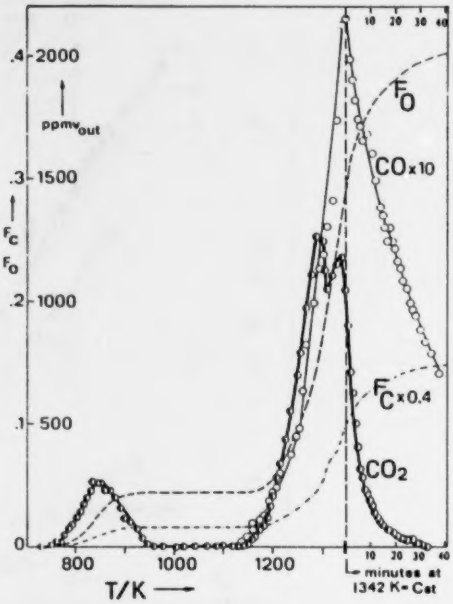


Figure 2. Reduction of CaS04 by graphite, under argon flow. 100 mg graphite + 500 mg CaS04

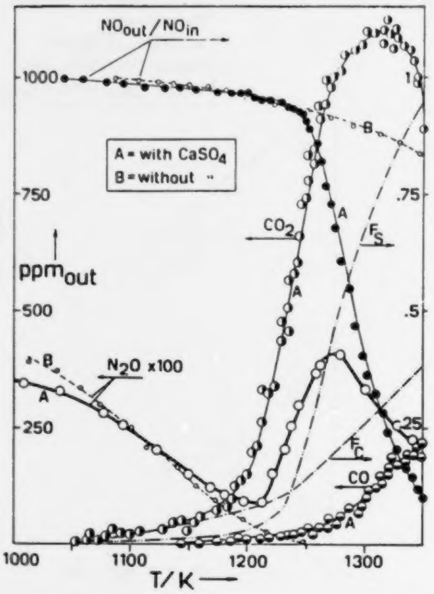


Figure 3. Formation of N20 from NO and CaSOR. 1240 ppm NO + 5 ppm NO2 in argon on 0.1 g graphite + 0.5 g CaS04

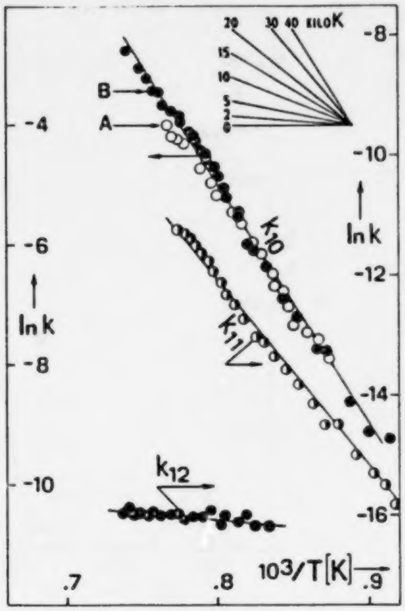


Figure 4. Overall rate constants of CaSO4 reduction by CO (K_{11}) and by graphite (k_{10}), the latter determined in the absence (A) or in the presence (B) of NO. Overall rate constant of N2O foramtion from NO and CaSOR (k_{12})

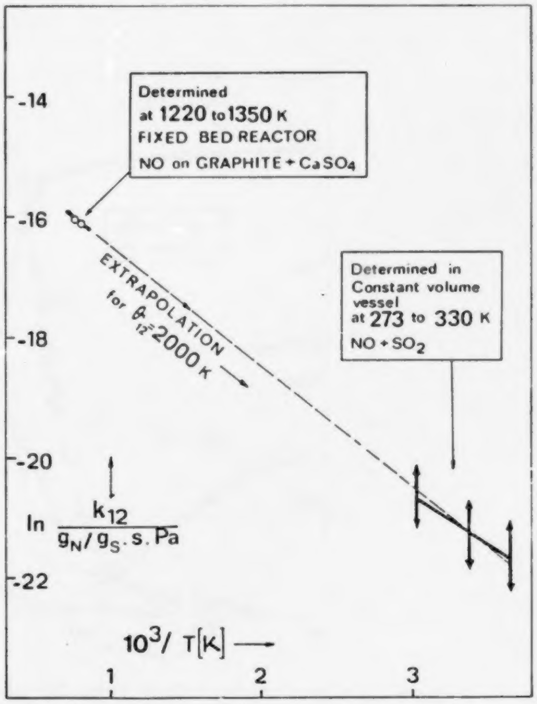


Figure 5. Comparison of k_{12} as determined at room temperature range and in the 1220-1350 Kelvin range

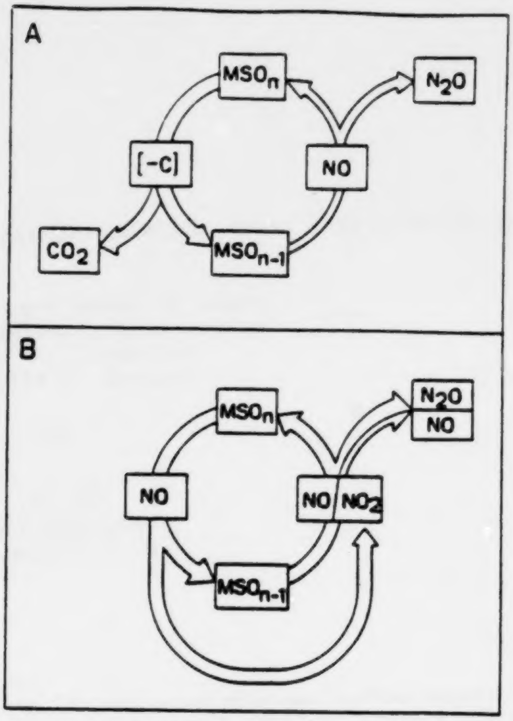


Figure 6. Schematical comparison of the overall mechanism of N2O formation from NO and sulfur compounds; A : with (-C) as a reductant; B : with NO as a reductant

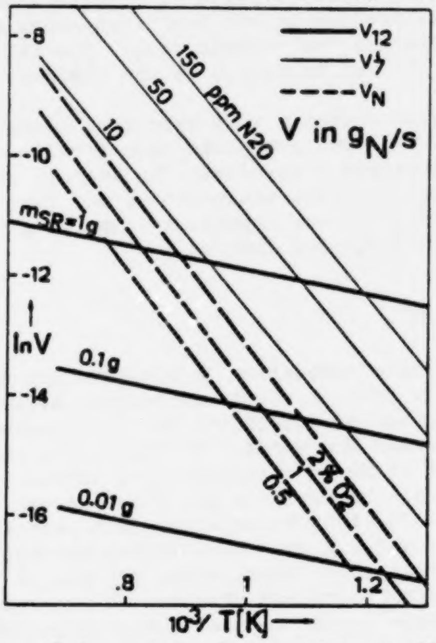


Figure 7. Comparison of V_{12} and V_N (from reference 5); Char from low volatile bituminous coal "Prosper"; P=0.1 MPa; m_C=1g; 1000 ppm NO.

FUEL NITROGEN MECHANISMS GOVERNING NO_x ABATEMENT FOR LOW AND HIGH RANK COALS

Jost O.L. Wendt and Arun C. Bose,
Department of Chemical Engineering,
University of Arizona,
Tucson, AZ 85721, USA

and

Klaus R.G. Hein,
RWE AG.,
Postfach 1461,
5010 Bergheim, FRG.

ABSTRACT

Fuel nitrogen mechanisms governing the efficacy of staged combustion were investigated for a low rank German Brown Coal and for a high rank Utah Bituminous Coal, burned in a downflow 2 kg/h laboratory combustor. Emphasis was on determination of the effects of coal rank on the rates of destruction of nitrogenous species in the fuel rich stage and on the subsequent conversion of these species in the burnout stage. Special experiments involving doped propane gas as a fuel allowed isolation of the dominant mechanisms in the coal runs.

This research revealed that reactions destroying NO and HCN were completely controlled by known gas phase reactions, and not by heterogeneous reactions, as has been hypothesized heretofore. The overall reaction is first order in NO and in NH_3. Furthermore, the late evolution of HCN into the bulk gas phase from both coals, at long time scales, was important in driving the gas phase reactions destroying NO and other nitrogenous species.

INTRODUCTION

Although staged combustion is a mature technology, its efficacy and performance are difficult to predict. Coal composition effects have been shown to be important, and several mechanisms describing the destruction of nitrogenous species have been proposed. Glass and Wendt [1] provided data on a single coal and showed that the destruction of NO at stoichiometric ratios (SR) of 0.8 and 0.4 could be interpreted using a simple homogeneous gas phase mechanism (based on Fenimore[2,3]) involving reaction of NO with NH_2 together with partial equilibrium approximations for the NH_i species and a global equilibrium assumption for OH. More recent work [4,5] has indicated that these conclusions may not be generally valid, and that heterogeneous reactions between NO and char may be important under coal combustion conditions, and that these depend on coal composition. The situation is further complicated by the fact that NO can be reduced on soot, and this has been suggested [6] as an additional mechanism to be considered, especially under very fuel rich conditions.

The purpose of the research reported here was to help resolve some of the discrepancies outlined above. To this end, a large data base consisting of aerodynamically well defined, time resolved profiles of major and minor species measured under simulated practical pulverized coal combustion conditions has been measured and analyzed. Effects of coal composition, stoichiometric ratio, temperature are explored and overall mechanisms appropriate for gas flames, where heterogeneous effects are absent, are compared to data for two widely different types of coal, where heterogeneous effects have heretofore been thought to be important. The two representative coals, for which detailed results are presented, are a German Brown coal and a Utah Bituminous coal, compositions of which are shown on Table 1, which also includes compositions of other coals used in this work. Behavior of these coals, as far as NO^x is concerned, can be thought to span coals of practical interest. The objective is to derive useful, practical models describing the destruction of nitrogenous species during the staged combustion of any coal.

EXPERIMENTAL EQUIPMENT

Laboratory Combustors

The downflow laboratory combustors used were designed to allow self-sustaining combustion, with no external heating, in a configuration that was representative of practical units in terms of characteristic times and temperatures, yet was still sufficiently well defined aerodynamically to allow the extraction of mechanisms and rates from the data. The experimental approach described here attempts, therefore, to bridge the gap between the more fundamental experiments of others and those from full or pilot scale coal combustion tests. In this way the mechanisms derived are both fundamentally correct and still directly applicable to general engineering practice.

Two kg/h of pulverized coal were transported by primary air, and subsequently mixed with preheated secondary air in a "pre-mixed" burner, following the design of Beer and Thring.[7] For doped propane gas runs, gas and air issuing from a concentric cylindrical duct were ignited after the water cooled "premixed" burner. NO additive was mixed with air and NH_3 was either mixed with air or injected via an axial port by a water cooled probe. One of the 15.2 cm ID combustors (Figure 1) was constructed of three concentric Zircar vacuum formed alumina cylinders surrounded by Kaowool bulk fiber and contained in a 80.4 cm OD steel shell. The radiant section was approximately 2m long, allowing residence times of 1 to 3 seconds depending on the coal and the stoichiometric ratio. The other combustor firetube was similar, but was hung from a frame, and allowed residence times of up to 10 seconds.

Temperature Measurement

In the determination of kinetic mechanisms, gas temperatures play a critical role. Axial gas temperatures were measured at various axial positions (ports), using a bare Type R thermocouple supported by a water cooled holder. The measured thermocouple temperatures were corrected for radiation heat loss, where the magnitude of this correction depends both on the measured gas temperature and on the wall temperature. Since measurements of the latter were sparse, it was calculated from a calibrated, one-dimensional, heat transfer model of the combustor. Because of the insulated nature of the combustor, the wall temperatures were usually within 20K of the corrected gas temperatures, and the maximum correction to the measured thermocouple temperature was always less than 35K. Had a more conventional insulating refractory been used, heat losses would have been greater and the temperature correction, therefore, also correspondingly greater.

The corrected temperatures reported here are, therefore, consistent with the measured axial temperature profile, with the few measured wall temperatures, with a local heat balance around the thermocouple and with another heat balance down the furnace.

Since previous work had shown that, under fuel rich conditions, particle temperatures did not differ much from those of the gas, the multi-wavelength infrared pyrometer utilized previously[1] was not used in this work.

Sampling and Analysis

Flue gas samples were withdrawn at the same locations (ports), using a water cooled, water quenched probe. The samples were analyzed to yield time-resolved profiles of major (O_2, CO, CO_2, H_2), hydrocarbon (CH_4, C_2H_2, C_2H_6) and nitrogenous (NO, NH_3, HCN) species.

After passing through a refrigerated knock-out pot, the sampled gases passed through in-line instruments for O_2, CO, CO_2 and NO_x analysis and also to a Perkin-Elmer Sigma 1B chromatograph outfitted with dual molecular sieve and Porapak T columns and thermal conductivity, nitrogen/phosphorous and flame ionization detectors. Emphasis was on accurate H_2 measurements, and for this, argon, rather than helium, was used as the carrier gas. Hydrocarbon analysis focused on CH_4, C_2H_2, C_2H_6 and C_6H_6, of which only first three were observed in the gas phase. Approximately one-half of the HCN was dissolved in the (metered) quench water, which was subsequently analyzed for HCN (after S^- precipitation) and for NH_3, using ion and gas electrodes respectively. These data were then converted to ppm (wet) values in the flue gas. H_2O concentrations were calculated from a hydrogen element balance. Solid carbon residue was calculated from a carbon element balance and was also collected in the knock-out pot. An independent oxygen element balance was closed, usually to within 5%, and this confirmed that all the data were consistent. Residence times were calculated using measured flue gas compositions, corrected temperatures and calculated molar flue gas rates.

RESULTS

Results from many experiments are presented, and each block of results immediately suggests certain conclusions. Rather than combine all the discussion in a separate section, we have, for the sake of clarity, have chosen to analyze the results as they are presented.

Staged Combustion

Figure 2 shows time resolved profiles of NO, NO + HCN and NO + HCN + NH_3 (TVFN) through the primary fuel rich ($SR = 0.57$), and through the staging point at 2.5 seconds residence time, yielding overall $SR = 1.21$. Shaded symbols denote data taken with second stage air injection, open symbols without air injection. Results are shown for the Utah Bituminous coal, and the effect of staging temperature is investigated by comparing data obtained when the second stage air was preheated (circles), to those when the second stage air was cooled (squares). The following conclusions can be drawn: 1) second stage NO is less than what would be predicted by 100% conversion of Total Volatile Fuel Nitrogen (TVFN); 2) second stage NO decreases with cooling at the staging point; and 3) the destruction of nitrogenous species in the first stage clearly plays a critical role in determining overall staging effectiveness. Therefore, the remainder of this paper focusses on mechanisms occurring in this crucial first stage. A low rank coal gave very similar results to those for the Utah coal, but with the important differences in the first stage, as described below.

First Stage Mechanisms

Figures 3, 4, and 5 show time resolved profiles of major and minor species through the primary fuel rich stage for the German Brown coal, the Utah Bituminous Coal and doped propane gas. Conditions are as shown on the figures. Important differences between each of these figures emerge: 1) for both coals the HCN profile did not decay down the combustor while for the doped propane it did; 2) the German Brown coal yielded higher quantities of NH_3 then HCN while the converse was true for the Utah coal.

These results then suggested the following issues to be addressed: 1) is the difference in nitrogenous speciation between coals a result of the different temperatures at which they burn, or is it due to an inherent property of coal composition? 2) can a unified model predict the decay of nitrogenous species for all coals and doped gas runs, or are heterogeneous reactions important for the coal experiments?

The first issue is addressed in Figures 6 and 7, in which the German and the Utah coals were burned at various temperatures, achieved by O_2 enrichment or N_2 dilution as shown. It is clear that the difference in N-speciation is not due to Temperature differences alone, but due to an inherent property of coal composition. For both coals, HCN is formed rapidly. Other data, not presented here confirms that even for the German coal HCN appears before NH_3. Therefore, the subsequent difference in N-speciation must be due to the different chemical environments each coal imposes on the gas phase. It is also noteworthy, that in all cases, the first stage should be as hot as possible for maximum destruction of bound nitrogenous species. Therefore, these results, when combined with those presented in the previous section, suggest that efficient staged combustion can be achieved with a hot (and long) first stage, coupled with rapid cooling at the staging point.

The second issue is addressed first by correlating NO destruction rates for all coal and gas runs using an empirical correlation (based on fundamental mechanisms), and second, by developing a fundamental but global kinetic model that in a unified way can describe all the NO destruction rate data for both gas flames, where heterogeneous effects are absent, and coal flames, where they might be present.

Empirical Model. Using the gas phase chemistry of References 8 through 13 as a guide, one can assume that, in the gas phase, the destruction of NO occurs through reactions with N, NH, and NH_2. Use of the following partial equilibria,

$$NH_{i+1} + OH \rightleftharpoons NH_i + H_2O \ , \tag{1}$$

and a global equilibrium for OH,

$$2OH + H_2 \rightleftharpoons 2H_2O \ , \tag{2}$$

yields:

$$-\frac{1}{(NO)}\frac{d(NO)}{dt} = (NH_3)\left[k''_1/(H_2)^{1/2} + k''_2/(H_2) + k''_3/(H_2)^{3/2}\right] . \tag{3}$$

This expression suggests the plots shown on Figures 8 (Utah coal and gas) and 9 (all other coals), where open symbols represent data and closed symbols represent predictions based on Equation (3), where the apparent rate coefficients are combinations of literature values of elementary rate coefficients and appropriate equilibrium constants. Different shaped symbols represent different experimental runs as shown. The data correlate well, but demonstrate a less severe temperature dependence than the model. The difference in apparent global activation energies cannot be attributed to errors in temperature measurement, which would merely tend to shift the experimental data laterally, but to discrepancies in the model. Although the gas data (and predictions) generally fall somewhat below those of the coal, this is due, we believe, to the higher levels of H_2 in the gas runs. Because of similarity between the gas and coal data, we conclude that homogeneous gas phase rather than heterogeneous chemistry controls the destruction of NO.

Figure 9 shows a composite plot for all the remaining coals, where each coal is denoted by a separate symbol, encompassing a range of temperatures and stoichiometric ratios. With the exception of data from the two low temperature runs for the German coal, the data both correlate reasonably well, and compare well to those for the Utah Bituminous #2 and the gas data shown on Figure 9. In general, NO destruction is first order in NO and NH_3 and exhibits a lower overall global activation energy than would be predicted from the partial equilibrium model (Equation 3). Eight data points from the two low temperature runs for the German coal, shown on Figure 6, fall close to the (OH equilibrium model) predictions and not on the general correlations for the vast majority of the data. If we attribute the general discrepancy between predictions and data to failure of the OH equilibrium assumption, then the surprising fit of the eight errant data points may be because stratification during these runs yielded local stoichiometries significantly richer than SR = 0.6, when global equilibrium may be reasonable for OH. It is noteworthy that Glass' SR = 0.8 data fits the general data trend, but his SR = 0.4 data lie on the equilibrium model predictions. Consideration of the whole picture, therefore, leads to the conclusion that provided SR $\geq$ 0.6, (1) homogeneous rather than heterogeneous reactions control NO destruction; (2) the rate for all coals can be correlated by an expression which includes the measured local NH_3 concentration, but is otherwise essentially independent of coal composition, and (3) the rate is first order in both NO and NH_3.

The least squares line shown on both Figures 8 and 9 represents:

$$\frac{1}{Y_{NH_3}} \frac{d \log_{10} Y_{NO}}{dt} \times 10^{-3} = 1.92 \times 10^{4} \exp(-11{,}400/T) \qquad (r^2 = 0.7) \tag{4}$$

and is compiled from all the data on both figures, but excludes the eight errant data points for the two questionable low temperature German Brown coal runs, Glass' data and the gas data. This correlation may be used to predict NO destruction rates for all coals if NH_3 concentrations can be estimated.

Kinetic Model. The global equilibrium assumption for OH can be relaxed by considering the kinetically limited destruction of OH via

$$OH + H + M \rightarrow H_2O + M \tag{5}$$

and partial equilibrium for H. Now Equation (3), describing the destruction of NO, is generalized to yield:

$$\frac{1}{(NO)} \frac{d(NO)}{d\,t} = -\,(NH_3)\, f_1\,[(OH),T] \tag{6}$$

where:

$$f_1 = 3.9272 \times 10^{17}\ T^{-1.6028} \exp(5276.5/T)\ (OH/(H_2O)$$

$$+\ 7.5701 \times 10^{15}\ T^{-0.91746} \exp(19650/T)\ (OH)^2/(H_2O)^2 \qquad (7)$$

$$+\ 3.2003 \times 10^{12}\ T^{-0.13392} \exp(39105/T)\ (OH)^3/H_2O)^3$$

and OH is above equilibrium and is a function of time (and ,in our system a function of temperature), and is calculated to yield for our conditions:

$$(OH) = (OH)_{Equil} \times 1.1 \times 10^{-4} \exp(15469/T) \qquad (8)$$

This model agrees with all the doped propane gas data, all the German Brown coal data, and all the Utah Bituminous coal data, as shown on Figures 10 through 14. In addition to predictions using this kinetic model for the super-equilibrium overshoot of OH, these figures also show predictions resulting from other less deterministic methods (not discussed here) of calculating this quantity. All methods yielded expressions very similar to Equation (8). Furthermore, Equation 8, which describes the super-equilibrium OH radical overshoot, also allows prediction of homogeneous HCN decay rates for the doped propane gas, but not for the coals, where HCN does not decay, and its concentration profile may be due to heterogeneous devolatilization effects.

CONCLUSIONS

NO decay for all the coals occurs by established gas phase mechanisms, and not by heterogeneous reactions, as has been proposed heretofore. Slow devolatilization of HCN from coals is important in supplying a pool of nitrogenous species which homogeneously react to form N_2 in the post flame. Nitrogenous species differ from coal to coal because of coal composition differences, not merely because of the different temperatures at which they burn. Optimum staging requires a hot primary zone followed by cooling at the point of second stage air injection.

ACKNOWLEDGEMENTS

This work was supported by the Pittsburgh Energy Technology Center, U.S. Department of Energy under Contract DE-AC22-84PC70771, administered by Energy and Environmental Research Corporation. The Project Manager was John Kramlich of EER and the DOE Project Officer was James D. Hickerson of PETC. RWE AG of West Germany provided the German Brown Coal and partial funding for investigation of its NO_x formation behavior. The authors would also like to acknowledge the assistance rendered by Terry Long and Robert Giattino in running the experiments and by Elizabeth Heddle in analyzing the data.

REFERENCES

1. Glass, J.W. and J.O.L. Wendt, Nineteenth Symposium (International) on Combustion, p1243, The Combustion Institute, Pittsburgh, Pa. 1982.

2. Fenimore, C.P., Combustion and Flame, 26, 1976.

3. Fenimore, C.P., Seventeenth Symposium (International) on Combustion, p661, The Combustion Institute, Pittsburgh, Pa. 1979.

4. Schulz, W., "Experimentelle Untersuchung der Bildung von Stickstoffoxiden bei der Kohlenstaubverbrennung", Dr.-Ing Dissertation, Ruhr-Universitat Bochum, FRG, 1985.

5. Kremer, H. and W. Schulz, Twenty-First (International) on Combustion, p1217, The Combustion Institute, Pittsburgh, Pa. 1986.

6. Lester, T.W., Personal Communication, 1986.

7. Beer, J.M. and N.W. Thring, "Some Measurements of the Rate of Combustion of Pulverized Anthracite in a Controlled Mixing One-Dimensional Furnace", Proceedings of Anthracite Conference Bulletin 75, Min. Ind. Exp. Sta., Penn State University, University Park, Pa., September 1961.

8. Haynes, B.S., Combustion and Flame, 28:31, 1977(a).

9. Haynes, B.S., Combustion and Flame, 28:113, 1977(b).

10. Branch, M.C., R.J. Kee, and J.A. Miller, Combustion Science Technology, 29:147, 1982.

11. Roose, T.R., Ph.D. Thesis, Stanford University, 1981.

12. Miller, J.A., M.C. Branch, W.J. McLean, D.W. Chandler, M.D. Smooke, R.J. Kee, Twentieth Symposium (International) on Combustion, p673, The Combustion Institute, Pittsburgh, Pa. 1984.

13. Glarborg, P., J.A. Miller and R.J. Kee, Combustion & Flame, 65:177-202, 1986.

Reproduced from best available copy.

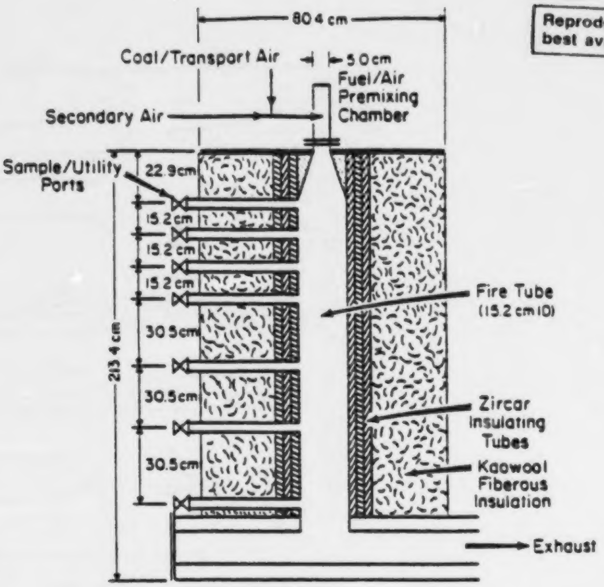


Figure 1. Experimental Combustor.

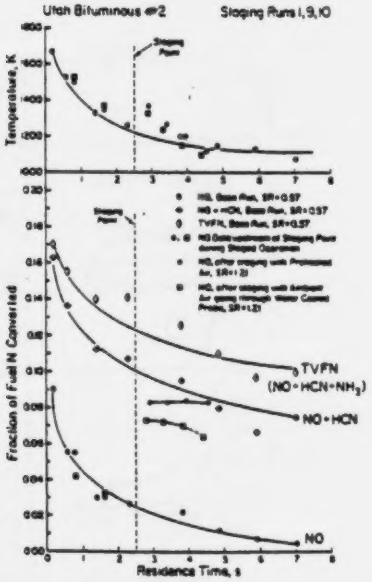


Figure 2. Temporal Profiles of Temperature and Nitrogenous Species in the First and Second Stages of a Staged Combustion Configuration. Utah Bituminous Coal.

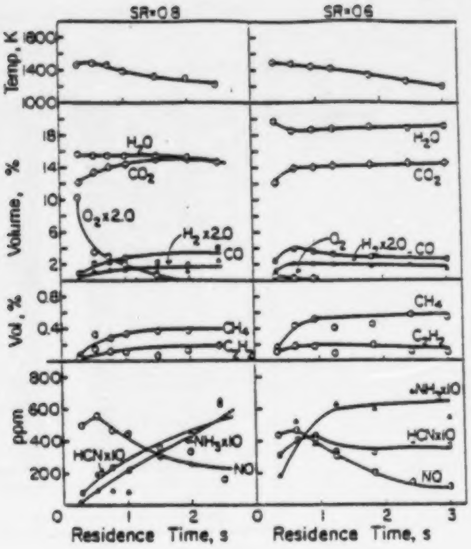


Figure 3. Base Case Profiles, Fuel Rich Stage: German Brown Coal.

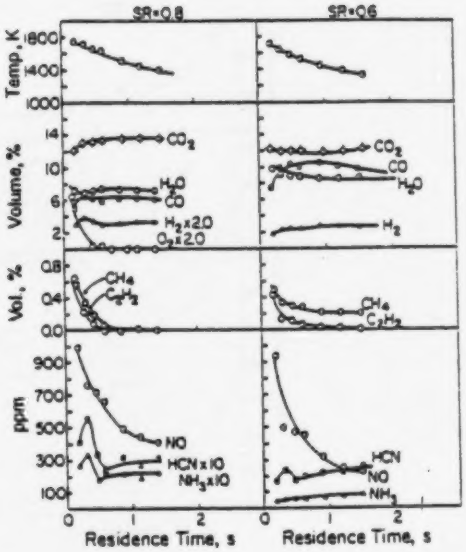


Figure 4. Base Case Profiles, Fuel Rich Stage: Utah Bituminous Coal.

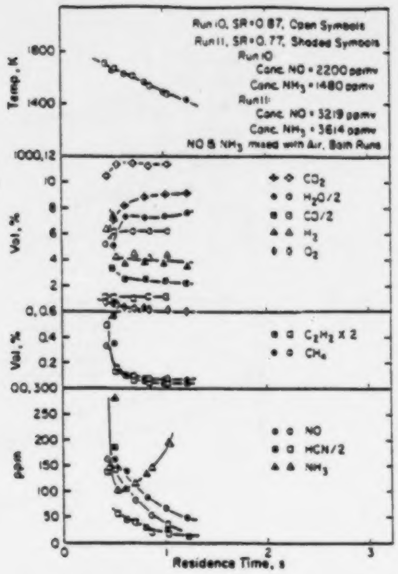


Figure 5. Base Case Profiles, Fuel Rich Stage: Doped Propane Gas.

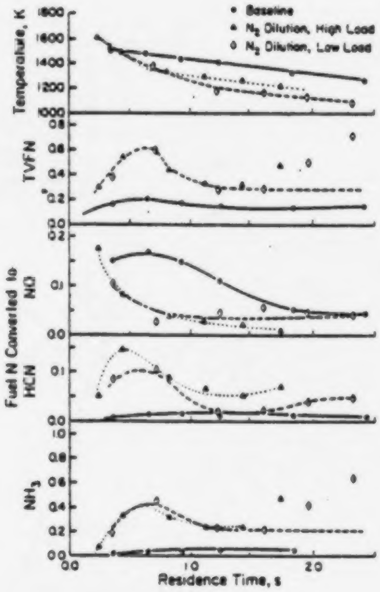


Figure 6. Effect of Temperature on the Speciation and Distribution of Nitrogenous Species: German Brown Coal, SR=0.6.

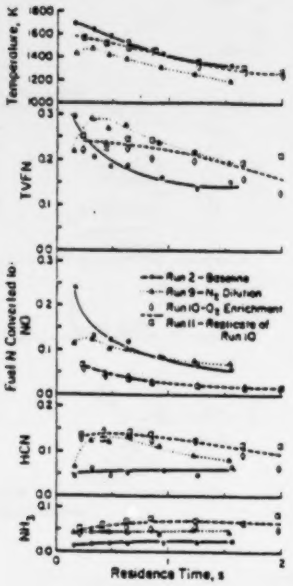


Figure 7.Effect of Temperature on Speciation and Distribution of Nitrogenous Species: Utah Bituminous Coal, SR=0.6.

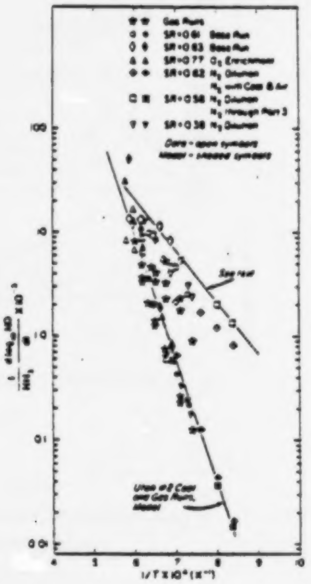


Figure 8. Comparison between Measured and Predicted NO Destruction Mechanisms. Utah Bituminous #2 and Doped Propane Gas Runs.

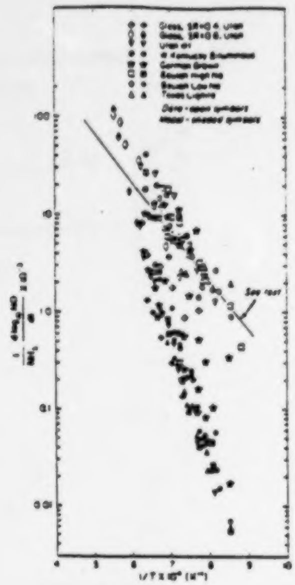


Figure 9. Comparison between Measured and Predicted NO Destruction Mechanisms. Seven Different Coals.

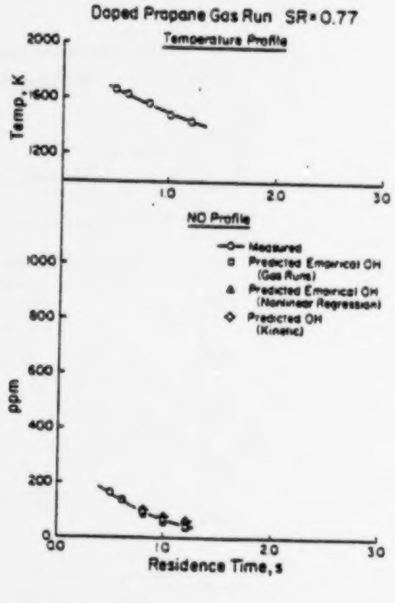


Figure 10. Measured and Predicted NO Decay Profiles: Doped Propane Gas.

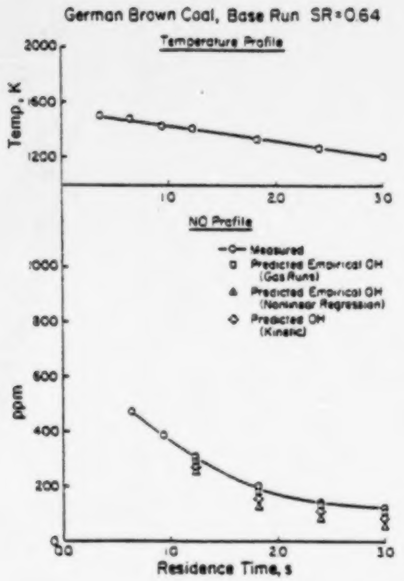


Figure 11. Measured and Predicted NO Decay Profiles: German Brown Coal, SR=0.64.

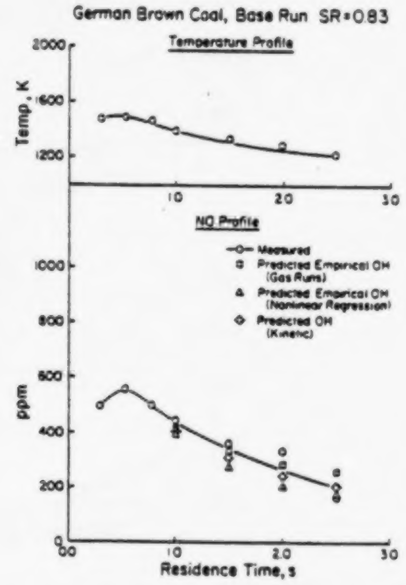


Figure 12. Measured and Predicted No Decay Profiles: German Brown Coal, SR=0.83.

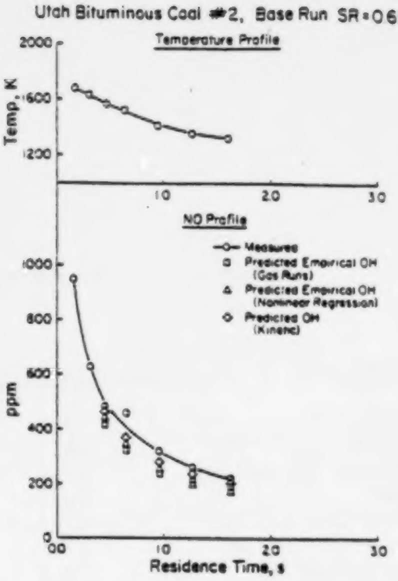


Figure 5.26. Comparison of Non-Equilibrium OH Models. Measured and Predicted NO values.

Figure 13. Measured and Predicted NO Decay Profiles: Utah Bituminous Coal, SR=0.61.

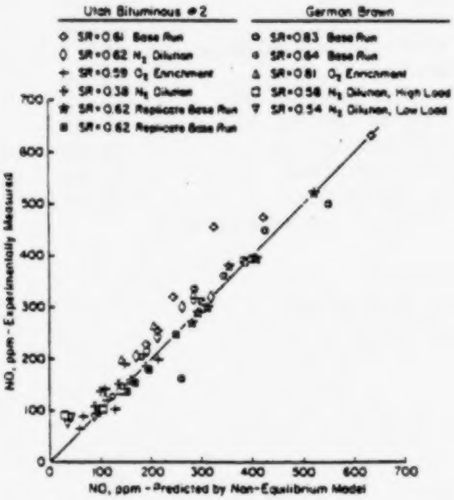


Figure 14. Measurements versus Predictions: All Cases.

Table 1: Pulverized Coal Compositions

#	Proximate Analysis	Volatile Matter	Fixed Carbon	Moisture	Ash
1	Utah Bituminous #1	39.2	47.4	4.5	8.9
2	Utah Bituminous #2	46.6	43.1	1.8	9.3
3	Western Kentucky Bituminous	41.8	46.9	3.0	8.6
4	Texas Lignite	34.5	30.2	14.0	21.3
5	Beulah Lignite Low Na. #1	38.3	35.3	13.1	13.3
6	Beulah Lignite Low Na. #2	37.1	37.1	17.8	8.0
7	Beulah Lignite High Na.	36.3	33.9	22.5	7.3
8	RWE German Brown Coal	48.9	13.4	28.8	8.8
9	RWE German Brown Coal Dried (from 74.4% moisture)	38.8	30.7	15.3	15.2

#	Ultimate Analysis (Dry, with Ash)	Carbon	Hydrogen	Nitrogen	Sulfur	Oxygen (Difference)
1	Utah Bituminous #1	70.87	5.11	1.64	1.03	12.08
2	Utah Bituminous #2	71.59	5.19	1.29	0.45	12.66*
3	Western Kentucky Bituminous	73.22	4.55	0.82	3.00	12.53
4	Texas Lignite	54.60	3.60	0.85	3.39	16.21
5	Beulah Lignite Low Na. #1	62.34	3.07	0.92	3.48	16.90
6	Beulah Lignite Low Na. #2	57.79	3.95	0.91	2.07	25.57
7	Beulah Lignite High Na.	59.80	3.90	1.08	1.02	24.78
8	RWE German Brown Coal	62.88	4.16	0.87	0.65	20.92*
9	RWE German Brown Coal Dried (from 74.4% moisture)	48.52	3.37	0.72	0.78	21.83*

---

*Analytically determined

METHANOL INJECTION - A NEW METHOD FOR NO_x AND SO_3 CONTROL

Richard K. Lyon
Energy and Environmental Research Corp
18 Mason Dr.
Irvine, CA, 92718

ABSTRACT

A theoretically predicted new homogeneous gas phase reaction has been demonstrated experimentally both on the laboratory scale and in pilot plant experiments. In this reaction the oxidation of trace quantities of methanol provides a rapid and nearly quantitative conversion of NO to NO_2 at temperatures greater than 700°C and a rapid, nearly quantitative reduction of SO_3 to SO_2. This reaction occurs under conditions which make its use in boilers and furnaces entirely practical and hence it provides the basis of a new process, the Methanol Injection process. Since the scrubbers now used to control SO_2 emissions can also efficiently remove NO_2, this new process may allow wet scrubbers to control both SO_2 and NOx emissions while protecting them from corrosion. Wet scrubbers necessarily operate at a temperature below the acid dew point. Thus when flue gas containing SO_3 enters the scrubber a fine mist of sulfuric acid is formed. Since the scrubber will typically only remove 50% of this acid mist, both the scrubber and the equipment downstream of it are vulnerable to corrosion. Since the Methanol Injection process selectively reduces SO_3 to SO_2, it can eliminate this problem.

The combination of Methanol Injection with either the Thermal DeNOx or Urea Injection processes appears particularly attractive, since the combined processes could achieve a high degree of NOx control and Methanol Injection would eliminate the NH_4HSO_4 fouling problems which presently hamper application of Thermal DeNOx and Urea injection.

INTRODUCTION

This paper describes a new technology that controls emissions of both NOx and SO_3. As has been discussed by Faucett, Maxwell, and Burnett[1], there have been a number of efforts to develop processes in which NO was oxidized to NO_2, with the NO_2 then being removed by a scrubber which also removed the SO_2. These efforts, however, all involved doing the NO to NO_2 conversion either with O_3 or ClO_2 and the expense of these reagents tended to make the overall process unattractive. More recently, Murakami and Izumi[2] have suggested using methanol oxidation to do the NO to NO_2 conversion. While this is potentially a much more attractive method of converting NO, there is the problem that both the examples and the claims of Murakami and Izumi are limited to temperatures below 700°C, i.e. limited to temperatures low enough so that NO_2 is not thermodynamically unstable with respect to decomposition to NO. Corresponding to this limitation to low temperature, the reaction times they show are in the range of 1.5 to 5 seconds. Such long reaction times are not typically available in most practical combustion systems.

While regulatory pressures to decrease NOx emissions are a relatively new event, the problems that the presence of SO_3 in flue gas can cause are of long standing. The combustion of sulfur containing fuels produces a flue gas in which typically 98-99% of the sulfur oxides are SO_2 with 1-2% present as SO_3. While SO_3 is thus trivial in terms of total SOx emissions, it still represents an important problem in terms of boiler and furnace operation. On cooling the SO_3 in the flue gas forms a sulfuric acid mist which can cause corrosion problems or, if the flue gas contains NH_3 from selective NO reduction, can form NH_4HSO_4 with resultant fouling problems. The former can be an especially severe problem in the operation of wet scrubbers. When SO_2 is removed from flue gas in a wet scrubber the gas temperature is necessarily below the acid dew point. On entering the scrubber the flue gas forms an acid mist. The mist particles, having an extremely low diffusion coefficient are not removed efficiently by the scrubber and tend to pass through it, causing corrosion problems downstream of the scrubber.

While this represents a significant problem for SOx control technology, NH_4HSO_4 formation is a problem for postcombustion NOx emission control. Several such processes are available, Thermal DeNOx, Urea Injection and Selective Catalytic Reduction, and all involve reducing NO in a manner that leaves traces of NH_3 in the flue gas. This can lead to NH_4HSO_4 formation downstream of the NO reduction zone with resultant fouling problems.

In this paper we report two discoveries: firstly that at temperatures greater than 700°C methanol oxidation can provide virtually complete NO to NO_2 conversion in reaction times as short as 0.05 seconds and secondly that while the methanol oxidizes the NO to NO_2, a second reaction occurs, a new homogeneous gas phase reaction in which methanol selectively reduces SO_3 to SO_2. Both these rapid reactions are highly selective in that ppm concentrations of SO_3 and NO are converted by quantities of methanol only slightly greater than stoichiometric in the presence of massive amounts of O_2. Prior to doing experiments the existence of this selective SO_3 reduction was predicted by computer modeling (3) and subsequent experiments were in reasonably good accord with the model's predictions.

These discoveries provide the basis for a new process for controlling both NOx and SO_3 and in this paper results for this process from modeling calculations, laboratory experiments and pilot plant tests will be reported. The potential advantages and limitations of this new process will also be discussed.

EXPERIMENTAL

The bulk of our experiments were done using the flow system shown in Figure 1. This flow systems consists of three subsystems: a system for blending fixed gases and vaporized liquids, a reactor, and an analytical train.

The gas blending system is a set of rotameters using the dilution blending method which allows preparing flowing gas mixtures of several components, the amount of each component being accurately known and readily varied in the range of several percent, down to a few ppm. Controlled amounts of CH_3OH vapor were added to the flowing gas mixture by passing N_2 at a measured flow rate through a saturator filled with methanol and kept at a controlled temperature (usually -16°C) and mixing this methanol containing flow with the main flow.

As shown in Figure 1, the addition of H_2O and SO_3 to the flowing gas mixture is done just upstream of the reactor. A dilute aqueous solution of H_2SO_4 is pumped via a precision metering pump to a vaporizer. The rate of pumping is chosen so as to provide the desired value of $[H_2O]$ in the gas mixture. On vaporization and heating above 300°C, H_2SO_4 is converted to H_2O and SO_3 and the concentration of H_2SO_4 in the solution is chosen so as to provide the desired value of $[SO_3]$ in the gas mixture going into the reactor. The construction of this system is such that the acid and its vapors never see any materials other than quartz and Teflon.

Once the appropriate gas mixture is prepared, it goes into the reactor, a length of quartz tubing inside a three zone electric furnace. This quartz tube reactor has three sections, an input leg of 1 mm ID, a center section of 10 mm ID and an outlet leg of 1 mm ID. The lengths of these three sections are chosen in such a manner that the input and outlet legs are in the portion of the electric furnace in which there is a temperature gradient and the center section is in the portion of the furnace in which the temperature is uniform. The reactor thus provides an accurately defined time-at-temperature.

After leaving the reactor, the flowing gas mixture is analyzed. NO, CO, SO_2 and O_2 were measured respectively by a Thermoelectron Chemiluminescent NOx meter, a Thermoelectron Gas Filter Correlation CO analyzer, a Thermoelectron Pulsed Fluorescence SO2 analyzer, and a Teledyne O2 analyzer. The first three of these instruments were calibrated daily with calibration gas mixtures purchased from Matheson, while laboratory air was used to calibrate the fourth.

Three different procedures were used to determine $[SO_3]$ in the post reaction gases. In procedure A a sample trap is used. The inlet end of this trap is inside the three zone electric furnace so that the gases entering the trap are at a temperature well above their dew point. The body of the trap was immersed in boiling water. As discussed by Wendt et al.[4] SO_3 may be quantitatively recovered from flue gas by condensation as H_2SO_4 at 90 to 100°C. By using the three way valve the entire gas flow was passed through this hot trap for a predetermined time, after which all flows were stopped and the amount of H_2SO_4 collected was measured by the procedure of Fritz and Yamamura (5), i.e., by titration with an 80% alcohol/20% water solution of barium perchlorate with thorin indicator. This sampling procedure has the advantage of eliminating several potential sources of error, i.e. the fraction of SO_3 remaining in the post reaction gas is simply the amount of H_2SO_4 collected in the trap divided by product of the rate at which the precision metering pump inputs acid and the collection time.

In procedures B and C the extent to which the input SO_3 was converted to SO_2 was determined for reaction mixtures in which SO_2 was not initially present by measuring the amount of SO_2 produced by the reaction with the Pulsed Florescence SO_2 meter. In procedure B, then, the conversion of the SO_3 was calculated as the ratio of SO_2 output measured by the SO_2 meter to SO_3 input calculated from the known rate at which the metering pump delivered sulfuric acid to the boiler.

In procedure C a converter was used, i.e. the setup shown in Figure 1 was changed so that on exiting the reactor the flowing gas mixture could be sent either to the SO_2 meter as shown in Figure 1, or sent via heated lines to a converter, a tube packed with platinum catalyst and heated to 1000°C, and then sent to the SO2 meter. In this manner it was possible to measure both [SO_2] in the post reaction gases and the sum of [SO_2] and [SO_3]. Also in procedure C the metering pump and boiler shown in Figure 1 were replaced with a unit that allowed the flowing gas mixture to pass over concentrated H_2SO_4 at elevated temperatures. By controlling the temperature the amount of acid vaporized into the gas mixture could be controlled. This allowed doing experiments with gas mixtures that contain no water vapor other than that which was formed by reaction.

As discussed in detail below, computer modeling studies showed that when methanol oxidizes in mixtures containing NO and SO_3 the NO is converted to NO2 while the SO_3 is reduced to SO_2, and that the optimum conditions for the two reactions tended to be the same. Since the measurement of NO to NO2 conversion is much easier than SO_3 to SO_2 conversion, this fact was useful in choosing experimental conditions for precise measurement of SO_3 reduction.

In addition to the above described laboratory scale experiments done with synthetic gas mixtures, a limited set of experiments were done with a 15.2 cm ID by 2.4 meter long refractory lined tunnel furnace fired with either natural gas or coal at 15 kW (Figure 2). The temperature profile in this unit matches the profiles typically found in utility boilers.

RESULTS

Figure 3 shows the results of a series of experiments in which methanol was oxidized at varying reaction times and temperatures in the presence of NO while Table 2 shows the results of a series of experiments in which various gas mixtures were passed through the reactor, and the concentration of SO2 in the post reaction gas mixture was measured by procedure A.

Two sets of experiments were done in which mixtures containing both NO and SO_3 were reacted with CH3OH and the amounts of NO converted to NO_2 and SO_3 reduced to SO_2 were measured as a function of the input CH_3OH concentration. One of these sets of experiments was done using procedure B and the other with procedure C. Figure 4 is a relative rate plot for the oxidation of NO to NO_2 and the reduction of SO_3 to SO_2, i.e. a log log plot of the NO and SO_3 conversions observed in these experiments.

Another set of experiments was done in which the NO to NO_2 conversion was measured for a gas mixture containing 225 ppm NO, 4.6% O_2, varying amounts of CH_3OH, either 0 or 2600 ppm SO2, and balance inert, reacting for 0.59 sec. at 601 °C. The presence or absence of the SO_2 was found to have no effect on the NO to NO_2 conversion.

A qualitative observation is also to be reported: it was found under a variety of conditions that the conversion of NO and SO_3 to NO_2 and SO_2 produces at least one mole of CO per mole of NO and/or SO_3 converted.

Figure 5 shows the results of combustion tunnel experiments in which methanol was injected in to flue gas produced by burning either natural gas, or natural gas doped with SO_2, or coal, and the conversion of NO to NO_2 was measured. It is to be remembered that in these experiments methanol was used in 1/1 ratio to NO, i.e. no methanol was supplied for the concurrent reduction of SO_3. Thus it is hardly surprising that the NO to NO_2 conversion was not as complete as was observed in the natural gas experiments.

Figure 6 shows the results of computer modeling calculations for the oxidation of NO by CH_3OH in the absence of SO_3 while figure 7 shows the computer model's predictions for the reduction of SO_3 by methanol in the absence of NO for varying temperatures
and reaction times. Calculations were also done for a variety of mixtures and conditions for mixtures containing both NO and SO_3. Figure 8, a log log plot of SO3 remaining versus NO remaining, shows data from these calculations.

DISCUSSION

Scientific Implications

The results above clearly show that it is possible to obtain nearly complete NO to NO_2 conversions at elevated temperatures at which NO_2 is thermodynamically unstable with respect to decomposition to NO. Given the limitations of the previous work this finding may be surprising, but it is to be recognized that this system is kinetically rather than thermodynamically controlled. As the temperature is increased the time needed for methanol oxidation to convert NO to NO_2 decreases. Thus, if the reaction time is shortened as the temperature is increased, it is possible to maintain conditions such that the initial conversion of NO to NO_2 goes to near completion while the NO_2 reconversion back to NO does not have sufficient time to occur.

The finding that the oxidation of methanol is capable of doing two apparently opposite things, selectively and quantitatively oxidizing NO to NO_2 while at the same time selectively and quantitatively reducing SO_3 to SO_2, may also prove puzzling at first glance. These opposite behaviors, however, are both results of the fact that methanol oxidation is an efficient method of producing HO_2 free radicals. By acting as an oxygen atom donor HO_2 can oxidize NO via the reaction NO + HO_2 = NO2 + OH and by acting as a hydrogen atom donor HO_2 can reduce SO_3 via the reactions, $SO_3 + HO_2 = HSO_3 + O_2$, $HSO_3 + M = SO_2 + OH + M$.

While the success of the computer modeling in predicting an entirely new chemical phenomenon is gratifying, it's to be realized that the agreement between the model's predictions and the experimental results is only qualitative. The model predicts that there will be a range of temperatures about 200°C wide within which the NO to NO_2 and SO_2 to SO_3 conversion can occur and that this "temperature window" will move to higher temperatures as the reaction time is decreased. While the experimental data confirm this, the model shows the temperature window at 0.1 seconds reaction time to be centered at 850°C while experimentally the 0.1 second window is centered at 725°C. Given that some of the rate constants used in the modeling have significant uncertainties small discrepancies of this kind are to be expected.

Similarly both the experimental data agrees with the model's prediction that a log log plot of the fractions of NO and SO_3 remaining should be a straight line, but the empirical slope found is somewhat different from that predicted by the model, again reflecting uncertainties in the rate constants used in the modeling.

In most respects the laboratory data for the conversion of NO to NO_2 by methanol are in agreement with the pilot plant data. However, it was observed in the laboratory experiments that SO_2 had no effect on NO to NO_2 conversion while the pilot plant data show an effect of having sulfur in the fuel. The explanation for this seeming conflict is, of course, that during the pilot plant experiments sulfur was present as both SO_2 and SO_3. Since there was only enough methanol present to reduce the NO, adding SO_3, which competes for the HO_2 radicals, naturally lowers the NO to NO_2 conversion.

Practical Implications

The experimental results reported above show new chemistry that allows the rapid conversion of NO to NO_2 (i.e. conversion on a time scale compatible with use of this chemistry for flue gas treatment) and allows the rapid reduction of SO_3 to SO_2. The extent to which this new chemistry will be useful in solving the emissions problems of boilers and furnaces depends on the answers to two questions: first is it practical to apply this new chemistry in boilers and furnaces and second, if it can be applied, is what it does useful?

The answer to the latter question depends on the situation. In situations in which only NOx control is needed, i.e. situations in which the flue gas is not scrubbed prior to discharge to the atmosphere, Methanol Injection would not be useful. If, however, the flue gas is to be scrubbed before discharge either for SO_2 or dust control, then methanol injection has two benefits. It can enable the scrubber to also remove NOx and it can protect the scrubber from corrosion by sulfuric acid mist. It's inherent in the operation of wet scrubbers that they cool the flue gas being scrubbed to a temperature below the acid dew point. Thus the SO_3 in the flue gas forms an acid mist in the scrubber, droplets in the submicron range. The efficiency of removing such droplets is typically only 50%. Consequently they can cause significant corrosion problems both in the scrubber and downstream of it. By reducing the SO_3 to SO_2 Methanol Injection would eliminate this problem.

While enabling an SO_2 scrubber to also control NOx emissions and eliminating corrosion due to sulfuric acid mist are potentially very useful, it is to be acknowledged that Methanol Injection has the disadvantage of causing modest emissions of CO. It is, however, important to keep this problem in prospective. In most applications the use of Methanol Injection to control NOx and prevent acid mist corrosion would cause CO emissions of less than 300ppm and those emissions would enter the atmosphere from the top of a tall stack. If an automobile has a fuel economy of 25mile/gallon and has its CO emissions controlled down to 2grams/mile, it is emitting 1300ppm CO at ground level.

One may tentatively answer the former question by comparing the chemistry of Methanol Injection with that of the Thermal DeNOx process[5]. In the Thermal DeNOx process one locates the point in a boiler or furnace at which the flue gas temperature is in a critical temperature range and at that point injects a small amount of NH_3 into flue gas. This causes a rapid homogeneous gas phase reaction to occur in which the NH_3 selectively reduces the NO to molecular nitrogen and water. While the Thermal DeNOx process has been successful in numerous commercial applications, there have been also situations in which it could not be applied. In some boilers and furnaces mechanical access is a major difficulty: one cannot conveniently install an NH_3 injection grid at the location in the unit required by the chemistry. In other units the problem is nonuniformity of the flue gas temperature: since Thermal DeNOx can only be applied over a modest temperature range, it can happen that at the location in a unit at which the average temperature is appropriate to Thermal DeNOx the range over which the temperature vary exceeds the process's tolerance. It is also possible that the reaction time available in a given unit may be inadequate: while the Thermal DeNOx chemistry is rapid it is not instantaneous and the process is not appropriate to situations in which some minimum amount of reaction time cannot be provided.

Analogous limitations are to be expected in a Methanol Injection process. In some units it may be difficult to install a methanol injection grid at the location required by the chemistry. It is, however, to be noted that since the optimum temperature for methanol injection is different from that for Thermal DeNOx, the required location of the injection grid is also different. Thus the processes compliment each other in that units which cannot provide an appropriate location for the injection grid of one process may still be able to do so for the other.

If one compares the data in Figure 3 with laboratory data for the Thermal DeNOx process[5], one finds that for both processes the temperature range is roughly 200°C. Thus, like Thermal DeNOx, Methanol Injection will be inapplicable in situations in which the flue gas temperature is highly inhomogeneous.

Continuing the comparison between Figure 3 and the data in reference 5 one notes that for the two processes each at its optimum temperature, the reaction time necessary for a given level of conversion, e.g. 80%, is 0.1 sec for Thermal DeNOx but only 0.024 sec. for Methanol Injection. Thus while Methanol Injection, like Thermal DeNOx, is subject to a minimum reaction time requirement, this requirement is significantly less severe for the former.

Overall, it seems fair to say that the chemistry of Methanol Injection involves quite similar limitation to those of the Thermal DeNOx process, and one would expect that this new process would, like Thermal DeNOx, be broadly but not universally applicable.

The combination of Thermal DeNOx and Methanol Injection may be particularly advantageous in situations in which high degrees of NOx control are needed. Methanol Injection could provide a substantial increment of NOx control over and above what is achieved by Thermal DeNOx. Moreover Thermal DeNOx has occasional problems with fouling due to NH_4SO_4 formation, i.e. the reduction of NO with NH_3 can leave small amounts of unreacted NH_3 in the flue gas. Downstream of the Thermal DeNOx reaction zone the unreacted NH_3 can combine with H_2O and SO_3 to form NH_4SO_4, a sticky and corrosive liquid which can foul heat transfer surfaces. Since Methanol Injection provides SO_3 reduction it can eliminate this problem, can solve the problem of byproduct production in the Thermal DeNOx process. Similarly if Methanol Injection is used downstream of Thermal DeNOx, the amount of methanol to be injected is greatly reduced, and the problem of producing byproduct CO is also largely removed.

ACKNOWLEDGMENT

This work was supported by the National Science Foundation under a Phase I Small Business Innovation Research grant, award number ISI-8760344.

REFERENCES

1. H. L. Faucett, J. D. Maxwell, and T. A. Burnett, Technical Assessment of NOx Removal Processes for Utility Application, EPA report EPA-600/7-77-127,p95 and following

2 N. Murakami, and J. Izumi, U. S. Patent 4,350,669, 1982

3 R. K. Lyon, U.S. Patent 4,743,436, 1988

4 J. Wendt et.al., 14th Symposium [International] on Combustion, p.898, The Combustion Institute, 1973

5 R. K. Lyon, U. S. Patent 3,900,559. 1975

Table 1

Demonstration of the Selective Reduction of SO_3 by CH_3OH

T,°C	t, sec.	Input Gas Composition, Balance N2,						Output Gas	
		O_2 %	H_2O %	CH_3OH ppm	NO ppm	SO_2 ppm	SO_3 ppm	NO ppm	SO_3 ppm
698	0.48	4.2	5.9	840	225	0	176	37	>0.1
698	0.48	4.2	5.9	840	225	0	176	11	>0.1
700	0.48	4.2	5.9	840	225	1785	102	8	6.8
699	0.48	4.2	5.9	840	225	1785	176	11	12.9*
699	0.48	4.2	5.9	840	225	1785	176	9.6	11.1*
698	0.51	4.5	6.3	445	0	1785	176		5.6
698	0.55	4.8	0	445	0	1924	0		>0.1
697	0.58	5.1	0	0	0	2022	0		>0.1
697	0.55	4.8	0	445	0	1924	0		>0.1
593	0.54	4.2	5.9	616	225	1785	176	NM	3.7
593	0.54	4.2	5.9	840	225	1785	176	NM	1.7
751	0.052	4.2	5.9	891	225	0	176	14.8	30.3
752	0.055	4.5	6.3	0	225	0	176	NM	165**

* In these runs in increase in $[SO_2]_{out}$ was measured and found to be 180-190 ppm, i.e. the sulfur balance was 101% based on total sulfur input and the differential balance (SO_3 accounted for divided by SO_3 input) was 113%.

**This is a blank run to demonstrate the efficiency of SO_3 recovery.

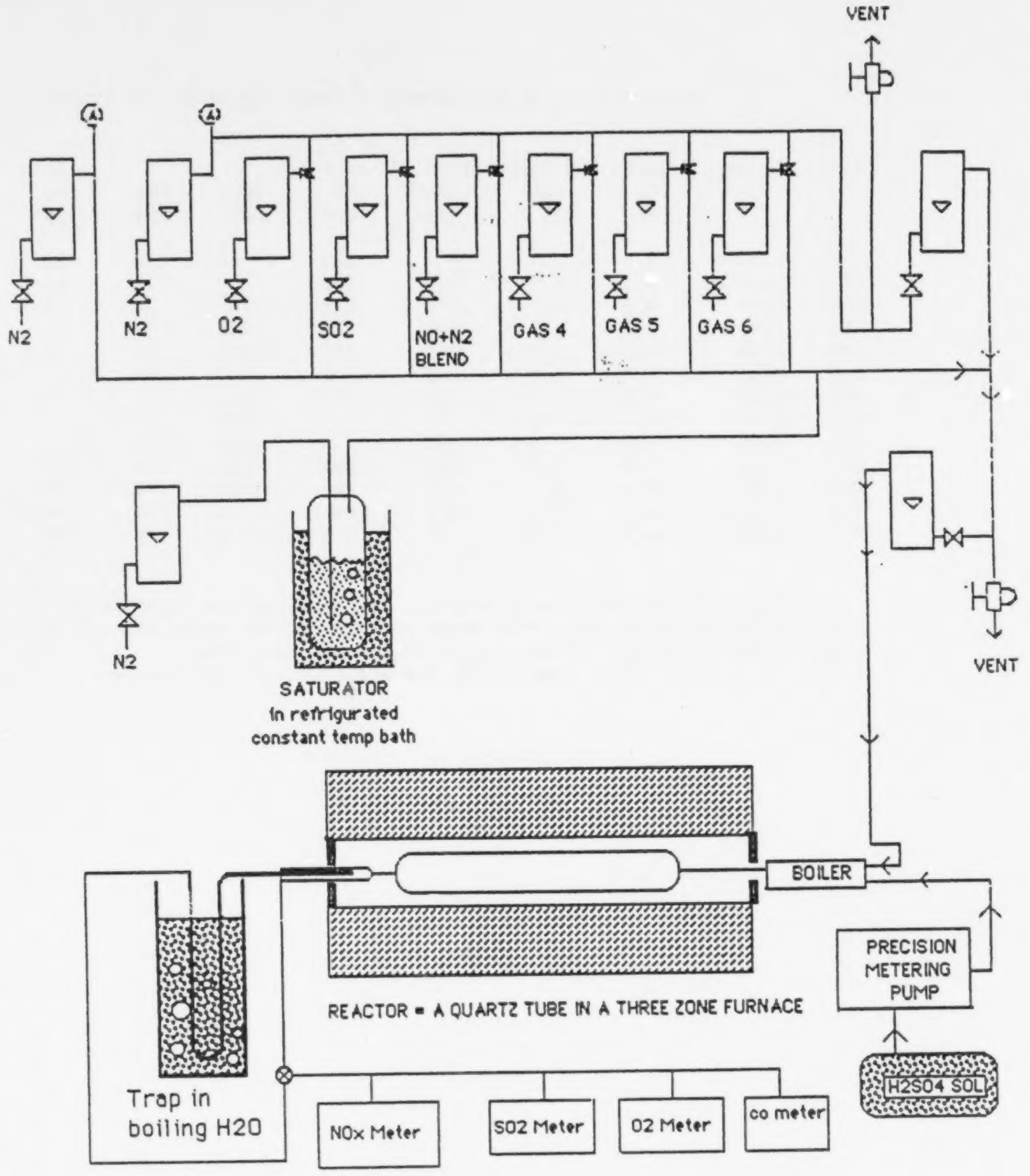


Figure 1 Precision gas kinetics flow system.

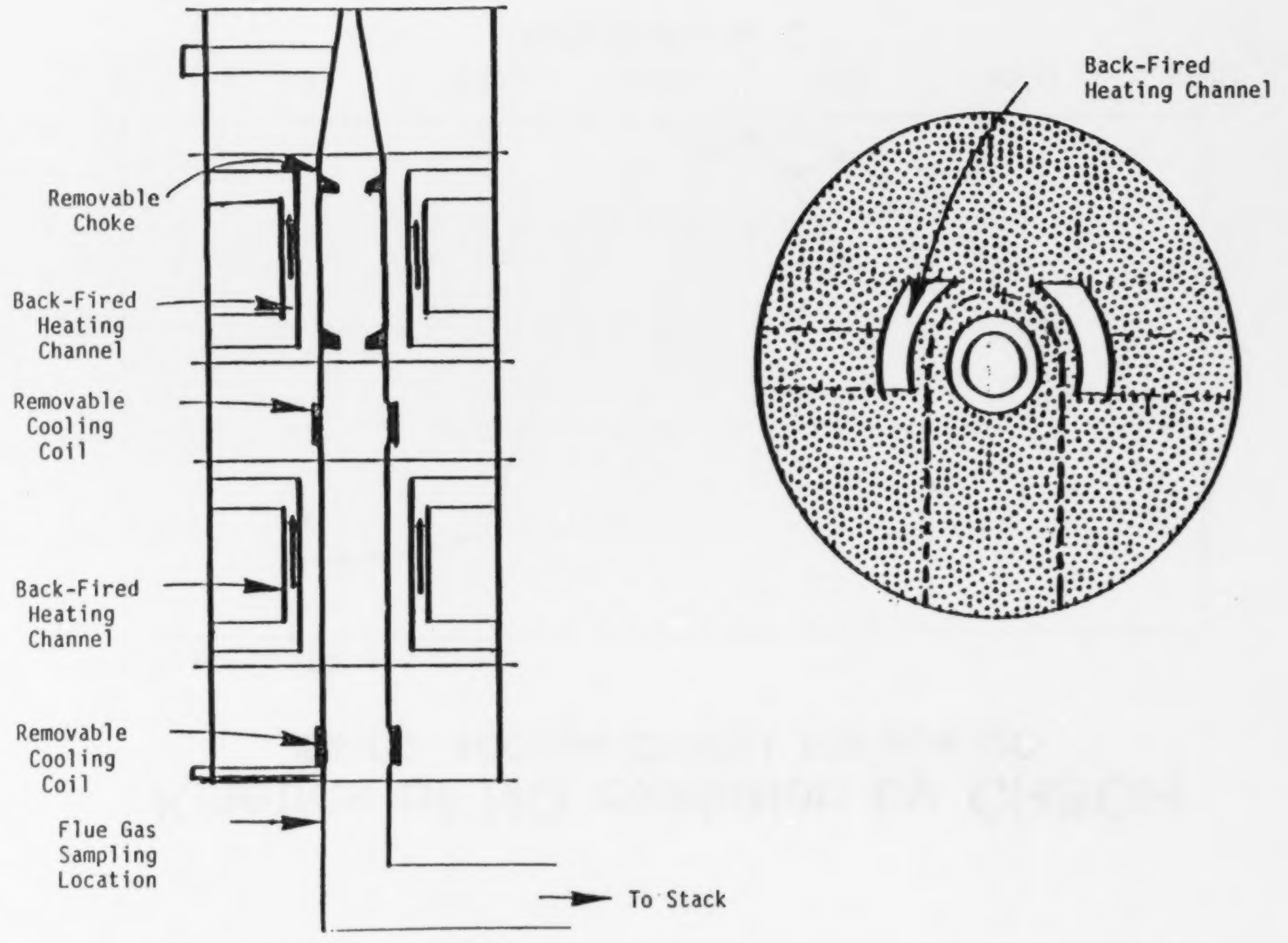

Removable Choke
Back-Fired Heating Channel
Removable Cooling Coil
Back-Fired Heating Channel
Removable Cooling Coil
Flue Gas Sampling Location
To Stack
Back-Fired Heating Channel

Figure 2 Cross-sectional views of the control temperature tower.

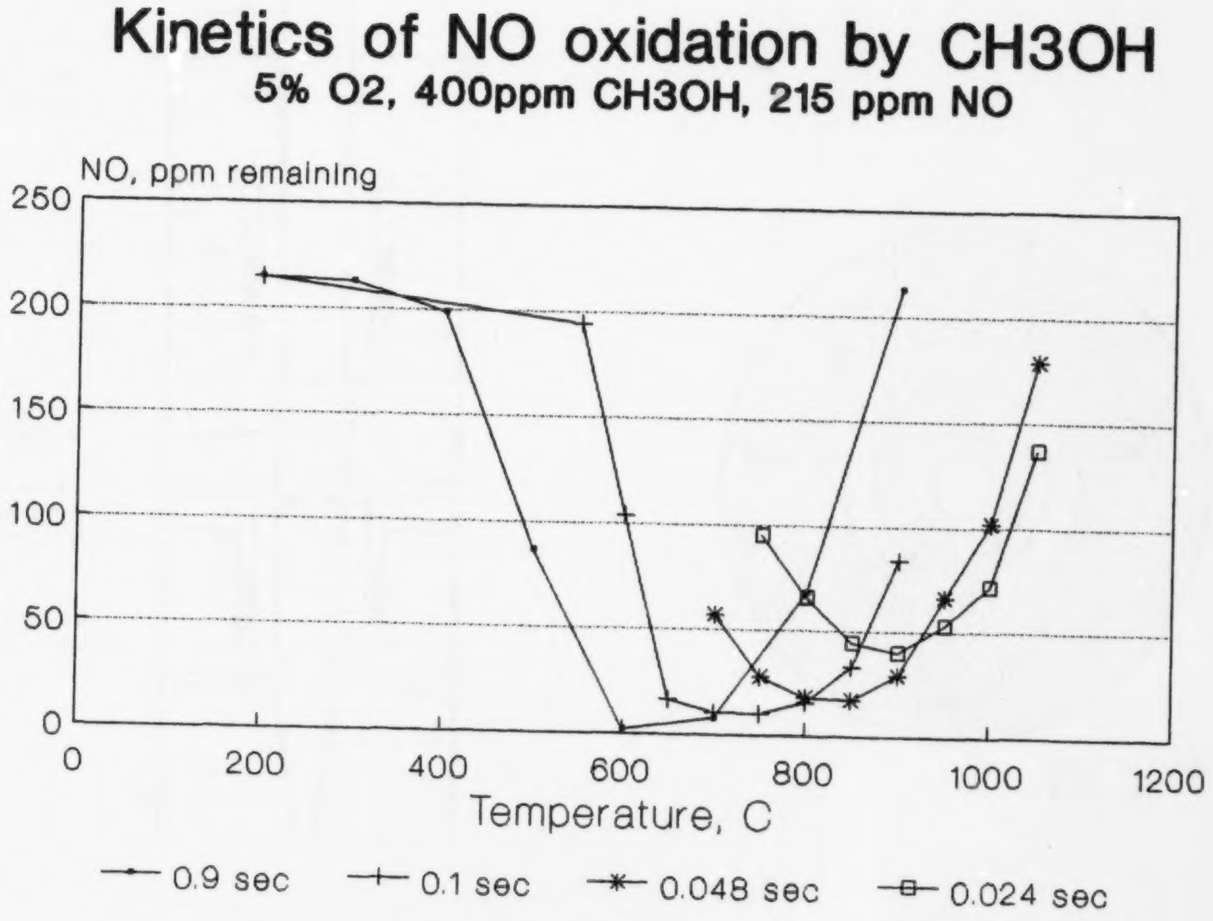


Figure 3 Kinetics of NO Oxidation

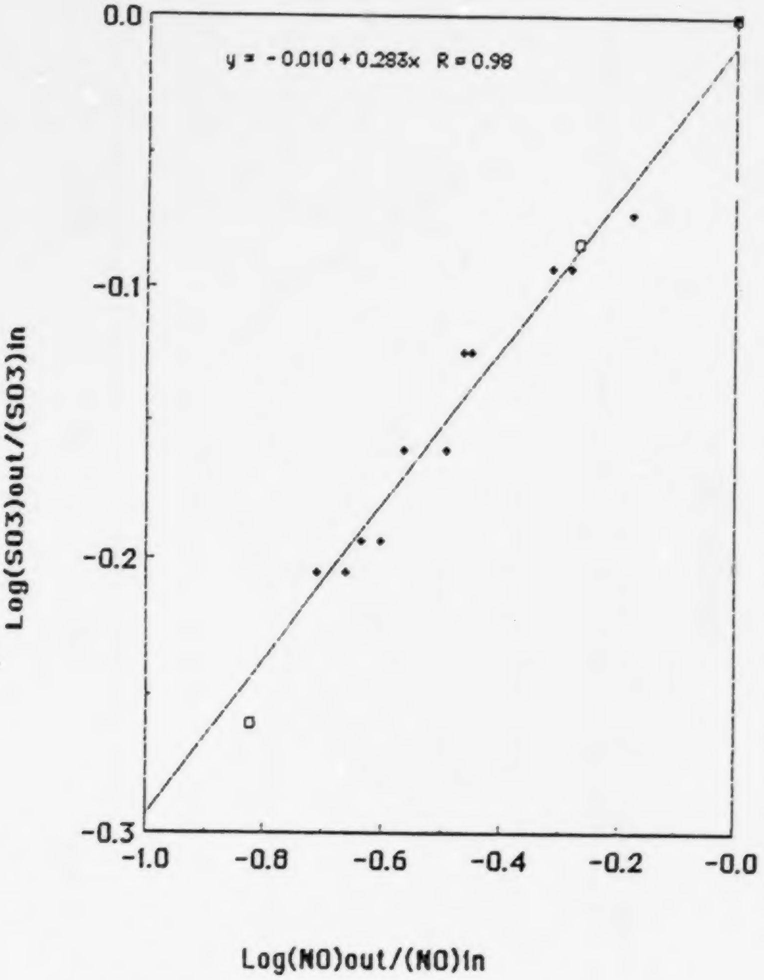


Figure 4 Experimental Data; log log plot of fraction NO remaining against fraction SO_3 remaining, solid points Method B, open points Method C.

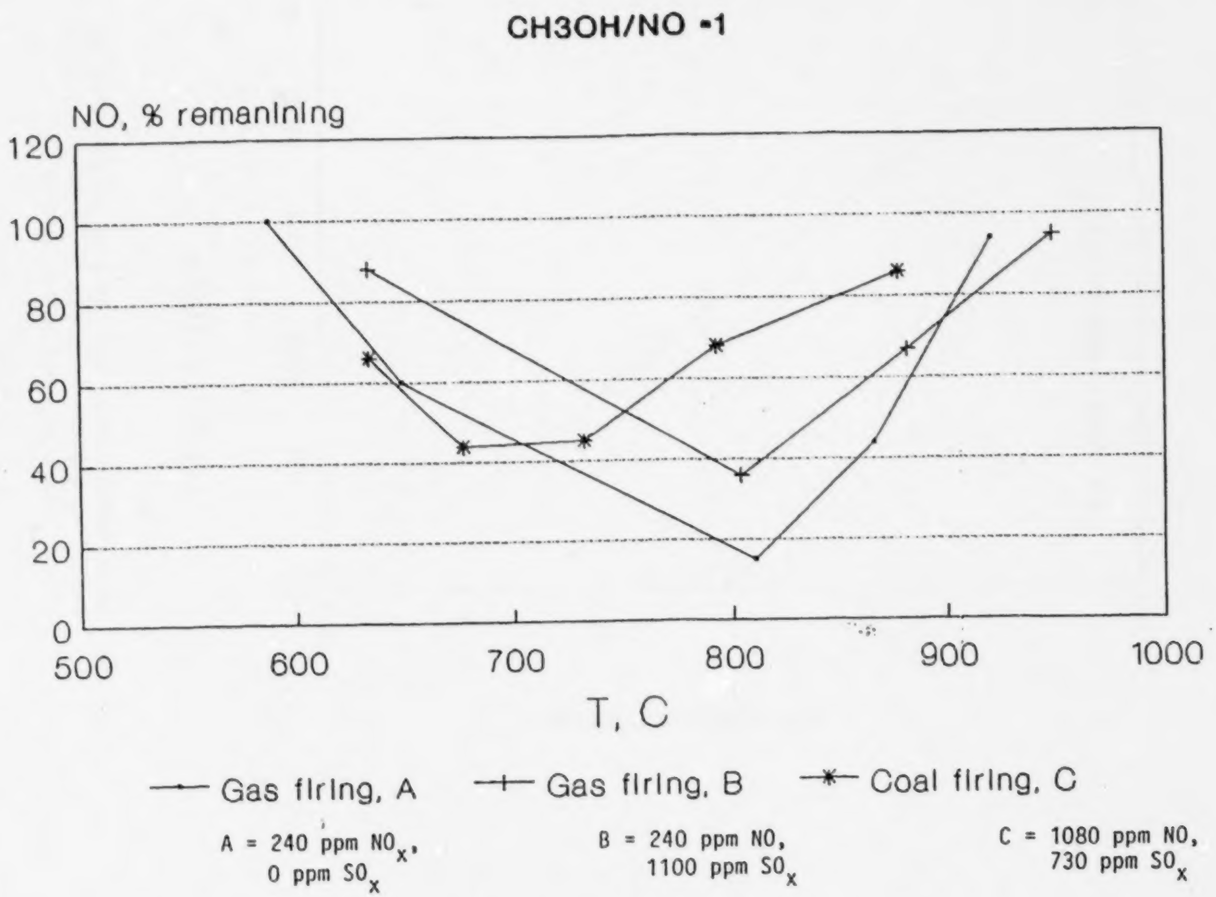


Figure 5 NO conversion during gas and coal firing.

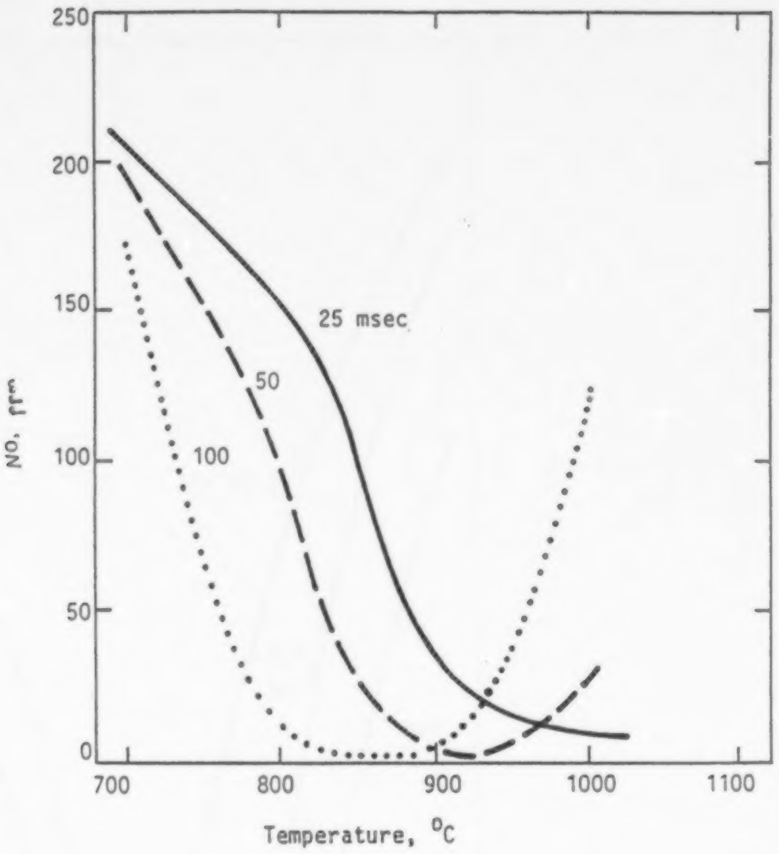


Figure 6 Modeling Calculations for Oxidation of NO by CH_3OH, 215 ppm NO, 400 ppm CH_3OH, 5% O_2, balance inert.

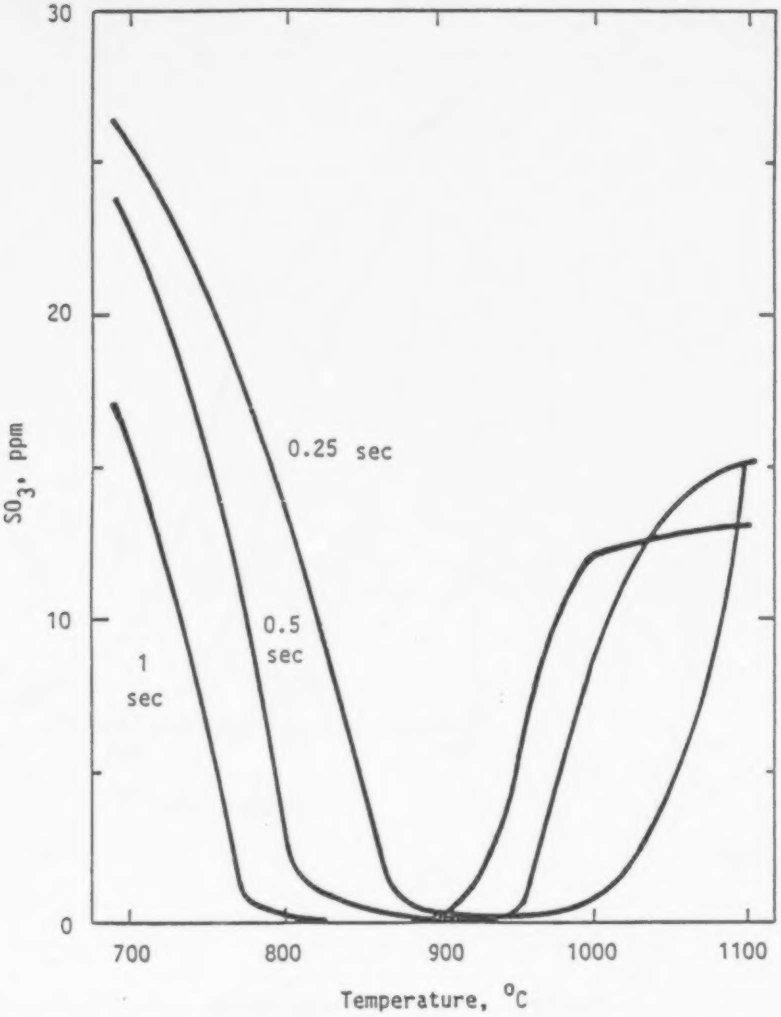


Figure 7 Predictions of the reduction of 30 ppm SO_3 in the presence of methanol oxidation under isothermal conditions. Reaction mixture = 4% O_2, 2000 ppm SO_2, 30 ppm SO_3, 40 ppm CH_3OH, balance inert.

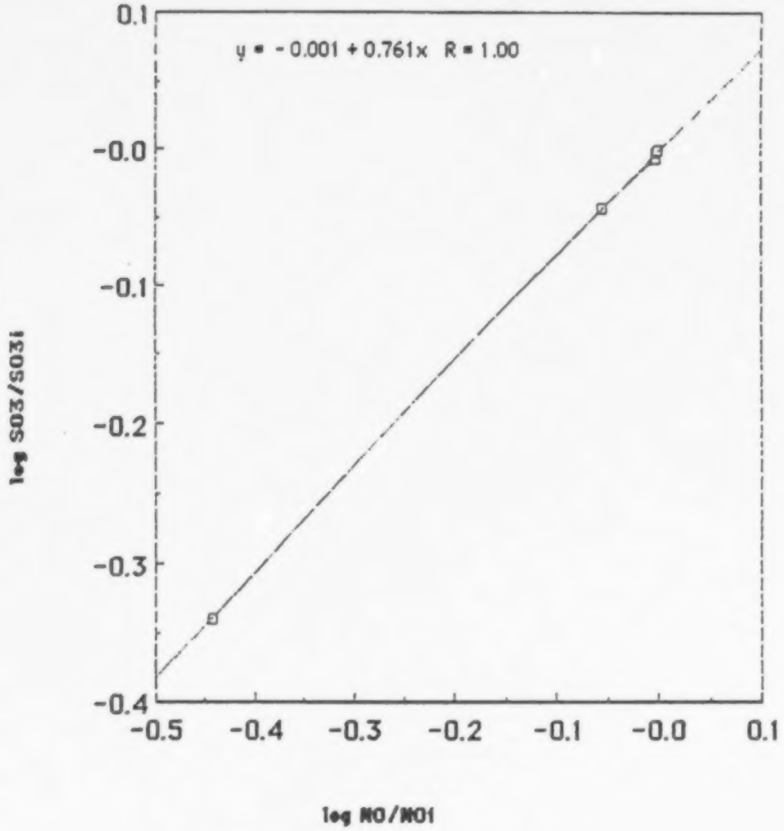


Figure 8 Data from computer modeling; log log plot of fraction NO remaining against fraction SO_3 remaining, data for calculations at 600°C with a reaction mixture of 10 ppm SO_3, 600 ppm NO, 800 ppm CH^3OH, balance inert.

Session 8

NEW DEVELOPMENTS

Chairman: E. Plyler, EPA

CATALYST POISONING IN THE SELECTIVE CATALYTIC REDUCTION REACTION

R. T. Yang, J. P. Chen and M. A. Buzanowski
Department of Chemical Engineering
State University of New York at Buffalo
Buffalo, NY 14260

and

J. E. Cichanowicz
Coal Combustion Systems Division
Electric Power Research Institute
Palo Alto, CA 94303

ABSTRACT

Activities of the V_2O_5/TiO_2 catalysts doped with various possible poisons have been measured with a simulated flue gas under SCR conditions. The strongest poisons are the alkali metal oxides; and the strength of the poison increases with the basicity, i.e., Cs > Rb > K > Na > Li. Arsenic is also a poison, but is weaker than all alkali metals except Li. The activities of all catalysts, both undoped and doped, are increased by the presence of SO_2. The experimental results indicate that Brönsted acid sites on V_2O_5 are responsible for the SCR reaction, and that the proton donicity of the V-O-H surface group determines the activity.

INTRODUCTION

The V_2O_5/TiO_2 catalyst has gained acceptance for the selective catalytic reduction (SCR) process, and has been tested commercially in Germany, Japan and other countries. The catalyst life is an important factor in the economics of SCR. Deactivation of the catalyst is caused mainly by the various "poisons" contained in the hot flue gas, which in turn, depends on the type of coal used in the combustion process. Very little is known about the poisons for the SCR catalyst. The purpose of this study is to obtain a systematic and fundamental understanding of the types of poison, as well as the poisoning mechanisms, with a specific emphasis on the possible poisons contained in American coals.

EXPERIMENTAL

The titanium dioxide powder (Degussa, P25) was mixed with distilled water at a ratio of 1.75:1 by weight, stirred thoroughly, and dried in an oven at 60°C for 24 hrs., followed by 120°C for 72 hrs. The dried mass was crushed and sieved to collect the 20-32 mesh fraction. This fraction was calcined at 600°C first in air for 1 hr. followed by 6 hrs. in helium at the same temperature. This support gave a BET surface area of 30 m^2/g.

The catalyst was prepared by incipient wetness impregnation. The TiO_2 support was impregnated with an oxalic acid solution of ammonium metavanadate, followed by drying at 120°C for 3-4 hrs. and calcination at 500°C in O_2 for 3 hrs. The V_2O_5 loading was 5% in all samples.

To prepare the poison doped catalysts, the 5% V_2O_5/TiO_2 catalyst was impregnated with the corresponding poison precussor solutions. For Li_2O, Na_2O, K_2O, Rb_2O and Cs_2O doped catalysts, $LiNO_3$, $NaNO_3$, KNO_3, $RbOOCCH_3$ and $CsOOCCH_3$ were used as the precussors. The impregnated catalyst was dried at 120°C for 3-4 hrs. and their calcined to decompose the nitrates and acetates.

A quartz tubular reactor was used for measuring the SCR catalyst activity. The reactor (2 cm I.D. and 30 cm long) was equipped with a thermocouple well and gas preheating section. The nitrogen was oxygen-free grade (< 0.5 ppm O_2); the NH_3 was anhydrous grade (99.99% purity); the NO purity was 98.5% min.; SO_2 purity was 99.9%; and O_2 was ultrahigh purity, > 99.99%. The simulated flue gas consisted of 1,000 ppm NO, 1,000 ppm NH_3, 2% O_2, 1% SO_2 (when used) and the balance N_2. The space velocity was 1,500 hr^{-1}. The flow rates were controlled by FM 4575 mass following a gas blending system (Linde Div.). The system is shown in Fig. 1.

The catalytic activity (NO_x conversion) was measured by

$$NO_x \text{ Conversion } (\%) = \frac{[NO_x]_{in} - [NO_x]_{out}}{[NO_x]_{in}} \times 100\%$$

The NO_x and NO concentrations were measured by a chemiluminescent $NO-NO_2-NO_x$ analyzer (Model 10, Thermo Electron Co.).

The rate equation for the SCR reaction is, as reported in a number of publications:

$$-\frac{1}{W}\frac{dC_{NO}}{dt} = kC_{NO}^{1}C_{NH_3}^{0}$$

The first-order rate constant, k, can be calculated for the plug-flow reactor by:

$$k = -\frac{F_{NO}}{C_{NO}W}\ln(1-X)$$

where C is concentration, F_{NO} is molar feed rate of NO, C_{NO} is inlet NO concentration, W is weight of catalyst, X is conversion, and t is time. This rate equation is applicable at O_2 concentration > 1% and at above stoichiometric NH_3/NO conditions. The temperature programmed reaction was performed at a heating rate of 10°C/min.

RESULTS AND DISCUSSION

Typical temperature-programmed reaction results are shown in Fig. 2 for the standard 5% V_2O_5 and K_2O-doped catalysts. At temperatures higher than 250°C, the oxidation of NH_3 (forming NO) became significant thus reducing the NO conversion. From these data, the first-order rate constants for the SCR reaction, k, can be calculated for temperatures below the peak temperature.

Figure 3 summarizes the activities of the standard 5% catalyst doped with various amounts of metal oxides as the poison.

The most prominent result is that alkali metal oxides are the most potent poisons. Moreover, the strength of the poison follows the order of basicity, i.e.

$$Cs_2O > Rb_2O > K_2O > Na_2O > Li_2O$$

50% Deactivation of the standard catalyst occurred at the following alkali metal/vanadium atomic ratios:

50% Deactivation: 0.07 (Cs/V); 0.12 (Rb/V); 0.14 (K/V);
0.31 (Na/V); 0.58 (Li/V)

This result shows the long-range effect of the highly alkaline metals, e.g., each Cs atom can deactivate (by 50%) approximately 14 V atoms. This result also reveals the severity of the alkalinity of American coals in the SCR reaction.

The effect of As on SCR has long been noted in the German experience. Our results show that, although As is also a potent poison, its poisoning strength is weaker than the alkali metals, except Li. Figure 3 also indicates that PbO is a strong poison whereas CaO is a weak poison.

Effects of SO_2

It has been known from pilot plant experience as reported in the literature that SO_2 deactivates the V_2O_5/TiO_2 catalyst by forming NH_4HSO_4 deposit on the catalyst. The results given in Table 1, however, showed a promoting effect of SO_2 on the catalyst activity for both undoped and poison-doped catalysts. The promoting effect of SO_2 may be interpreted as the enhancement of the acidity of the catalyst surface.

Table 1 also includes the activity data of $CuSO_4/Al_2O_3$. $CuSO_4$ is considered as a solid acid with Brönsted acid sites. The activity of $CuSO_4$ is similar to that of V_2O_5 at 300°C. However, it is much more active than V_2O_5 at higher temperatures (not shown in Table 1).

Active Sites and Possible Poison Mechanism

Extensive measurement on the chemisorption of NH_3 on the undoped and doped catalysts have been undertaken in our laboratory. The measurements were done at 200°C. A nearly one-to-one correspondence between the amount of NH_3 chemisorption and the SCR activity was obtained for all catalysts included in Fig. 3. However, a large amount of NH_3 chemisorption (corresponding to 21 $\mathring{A}^2/NH_3$ molecule) was also measured for the TiO_2 support, which has no SCR activity. These results indicate that NH_3 chemisorbs on all acid sites, including Lewis and Brönsted acid sites. It is known, however, that the chemisorption of NH_3 on TiO_2 is by Lewis acid and hydrogen bonding, and that NH_3 chemisorption on V_2O_5 is on Brönsted acid sites. Consequently, it appears that the Brönsted acid sites on V_2O_5 are responsible for the SCR reaction, which is likely in the form of -V-O-H groups. It follows that the donicity of H proton, i.e., the ease of breakage of the O-H bond, is the rate-limiting factor in the SCR reaction and determines the activity. The effect of the alkali metals appears to be dontating electrons to the surface and consequently strengthening the V-O-H bond. And such an effect could be a long-range one as indicated by the results with Cs_2O, which deactivates a large number of active sites by each Cs atom.

Table 1

Effect of SO_2 on NO Conversion and Rate Constant (k) for SCR at 300°C. (Other conditions are given in Figure 2).

	Without SO_2		With 1% SO_2	
Catalyst	Conv. %	$k \times 10^2$, $cm^3/g/s$	Conv. %	$k \times 10^2$, $cm^3/g/s$
5% V_2O_5/TiO_2(A)	98.0	10.38	99.2	12.82
0.74% CaO/A	97.2	9.49	99.2	12.82
0.32% Li_2O/A	91.4	6.52	99.1	12.63
0.68% As_2O_3/A	96.7	9.09	99.2	12.82
7% $CuSO_4/Al_2O_3$			99.2	12.82

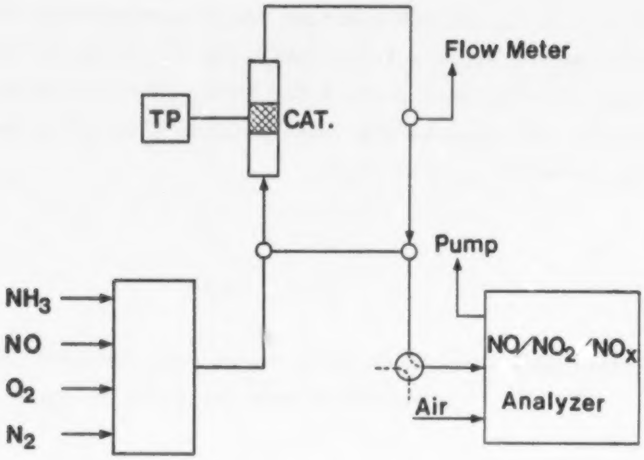


Figure 1. Schematic of experimental system. TP: temperature program/control. CAT: packed catalyst pellets.

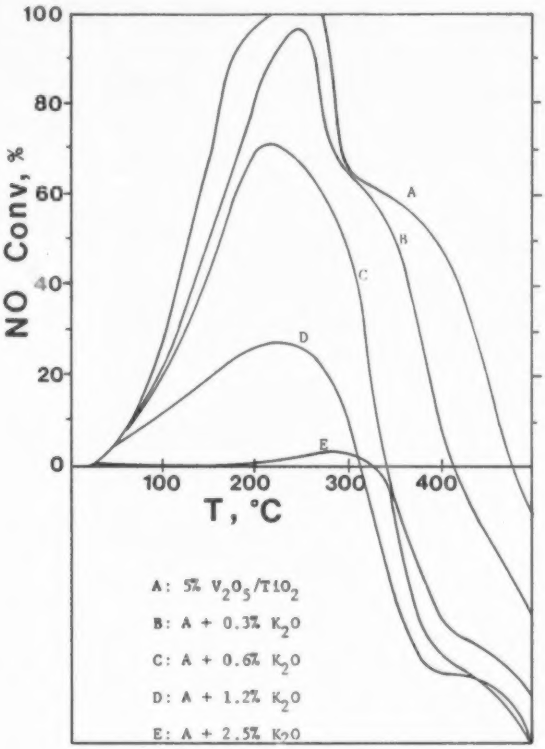


Figure 2. Conversion of NO in the SCR reaction on K_2O doped catalyst. NH_3 = NO = 1,000 ppm, O_2 = 1%, N_2 balance, GHSV = 15,000 hr^{-1}.

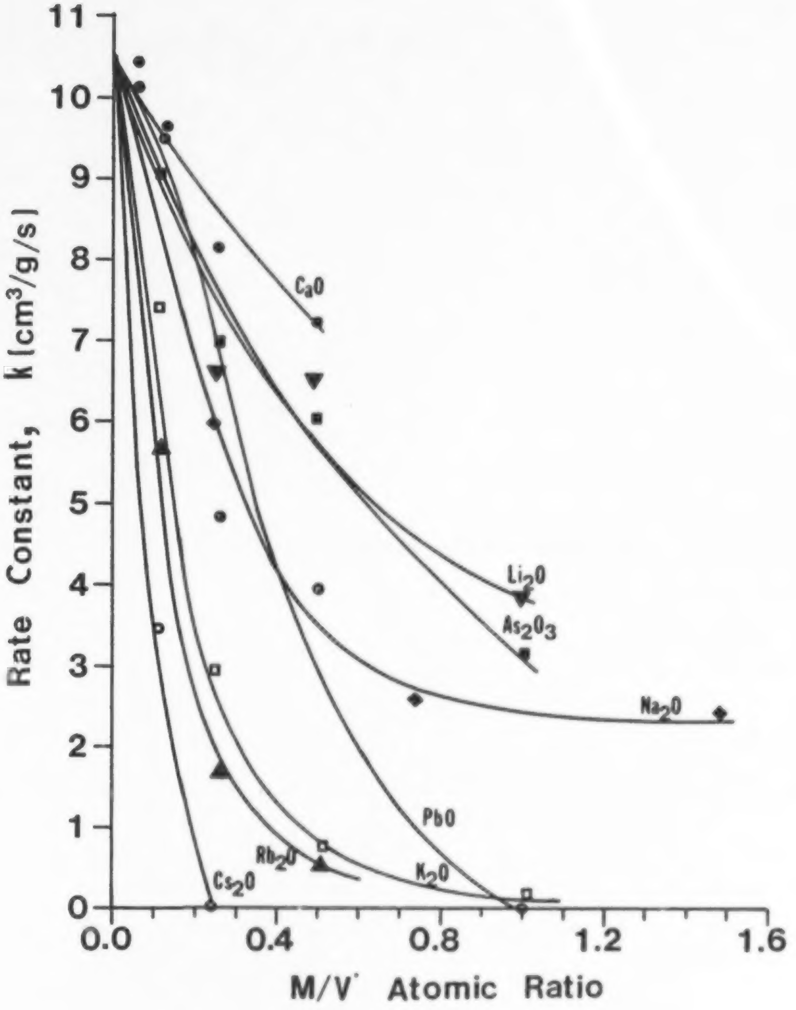


Figure 3. Activity (as indicated by rate constant) of 5% V_2O_5/TiO_2 doped with different amounts of metal oxides where M/V = metal/vanadium atomic ratio. Reaction condition: 300°C, NO = NH_3 = 1,000 ppm, O_2 = 2%, N_2 = balance, GHSV = 15,000 hr^{-1}.

CATALYTIC FILTER BAGS

Marie R. Kalinowski, Patrick F. Aubourg
Science and Technology
Owens-Corning Fiberglas Corporation
Technical Center
Granville, Ohio

ABSTRACT

Owens-Corning Fiberglas Corporation (OCF) has developed a catalyst-coated fabric for baghouse applications to simultaneously control particulates and NOx emissions. NOx is eliminated by catalytic reaction with ammonia. NOx reductions of 90% with low ammonia slip (< 10 ppm) are achievable. Bench scale tests conducted at OCF and at the University of North Dakota, Energy and Mineral Research Center have shown the merit of this system; this data will be presented. Eight hour tests were conducted on 8 X 11 inch coupons using flue gas from a coal-fired boiler. Conversion efficiencies of up to 93% were measured. Preliminary tests have also been conducted on small bags. Economic data will be presented.

Due to the very efficient use of the catalyst and combination of two functions into one unit, cost will be significantly lower than use of a commercial SCR (Selective Catalytic Reduction) unit and a particulate removal unit.

Introduction

Many techniques exist for the reduction of NOx emissions from flue gas streams of coal-fired boilers. Some methods, while relatively cost-effective, are incapable of high (> 80%) NOx removal. Others, with the potential for high NOx removal rates, result in large capital investments, high operating costs, or operational difficulties, making the processes unattractive.

Over the past several years, Owens-Corning Fiberglas Corporation (OCF) has developed a catalytic S-glass cloth capable of removing NOx at high efficiencies. When sewn into a filter bag, the cloth will also effectively filter particulate matter. There are several advantages to this concept: a two-in-one pollution removal device, resulting in space and cost minimizations; no undesirable by-products; an already-existent industry familiarity with baghouse technology; and, of course, NOx removal efficiencies in excess of 90%.

Laboratory data on a simulated flue gas stream at OCF indicated that removal efficiencies above 90% were indeed feasible. In order to evaluate the process in an operational flue-gas stream, OCF has worked with the Energy and Mineral Research Center (EMRC) at the University of North Dakota. The objectives of the work were to optimize the cloth's efficiency for NOx removal and to examine the effects of various operational parameters (stoichiometric ratio, coal type, etc.) on the removal efficiency.

How Does it Work?

In some respects, the OCF catalytic filter bag is similar to existing SCR (selective catalytic reduction) technology. It employs ammonia in the presence of a vanadia/titania catalyst for the reductions:

$$6\ NO + 4\ NH_3 \text{ --> } 5N_2 + 6\ H_2O$$
$$6\ NO_2 + 8\ NH_3 \text{ --> } 7N_2 + 12\ H_2O$$

Operating temperatures are also similar (650°F).

What makes the catalytic filter bag different is the form of the vanadia/titania catalyst. Instead of being supported on a honeycomb-like structure, the catalyst is coated and bonded directly on an S-glass cloth surface. Titanium isopropoxide and vanadium tri-n-propoxide oxide, sometimes called "sol-gel" materials, are used for the coatings. After coating, the sol-gels are air-dried, which hydrolyzes them, forming a highly porous layer. Low temperature curing drives off any residual organics and partially densifies the coating. The result is a catalytic coating--still highly porous, and strongly bonded to the glass surface. It has been estimated(1) that the OCF catalytic cloth would require only one-seventh the volume of a traditional SCR catalyst to achieve equal levels of NOx removal.

Experimental

All tests were conducted on a slipstream from the coal burning Particulate Test Combustor (PTC) at EMRC. Initially, filter bags were not available; therefore, a special slipstream sampler was constructed. A fabric sample, roughly 8 x 11 inches, was housed in an oven operating at 650 ± 25°F. After the filter the gas flow was split, with 10 scfh going to a sample conditioner and flue gas analyzers, and the balance of 20 scfh going to a gas pump and dry gas meter for control of the total flow. Ammonia was injected into the system well upstream of the sample point to ensure sufficient mixing into the flue gas stream prior to sampling with the slipstream sampler. Baseline operating conditions for the tests are listed in Table 1.

The filter bag trial used nine bags, each approximately 4 feet long and 7 inches in diameter. Glass cloth weight was approximately 14 ounces per square yard. Experimental conditions were similar to those used for the slipstream trial.

Results and Discussion

Conversion efficiencies for the first fifteen samples tested on the slipstream sampler ranged between 70 and 93 percent. Differences in conversion efficiencies arose from the amount of catalyst on the cloth, curing differences, and cloth weight variations.

These tests on swatches being extremely encouraging, it was decided to conduct tests on small filter bags.

Some problems were encountered during the early stages of the bag trial. Conversion efficiencies were low, averaging 50 percent. The reasons for the low conversion efficiencies were not immediately understood. Recent work has indicated that the silicones used as gasketing material attack the vanadia-titania catalyst and decrease conversion efficiency. After replacement of the original bags and regasketing the baghouse with Fiberfrax, conversion efficiencies averaged nearly 80 percent. After two days of operation, conversion efficiencies had not decreased and, equally important, no holes or tears were found in the bags.

A second set of slipstream samples was tested using a different coal. Baseline operating conditions are listed in Table 2. Conversion efficiencies averaged 86 and 93 percent for the two samples. The stoichiometric ratio of ammonia to NOx was also varied, and the ammonia slip was monitored. Results are plotted in Figure 1. The conclusion was that high conversion efficiencies could be obtained with minimal ammonia slip.

Economics

The key economic advantage of a catalytic fabric system lies in the fact that major, new and unfamiliar equipment would not be required and that a single device (a baghouse) could be utilized for the control of two major environmental pollutants: NOx and particulate matter. The utility industry has been required to control particulate matter for decades, and it has been documented that fabric filtration is the control method of choice.

Once the fabric filtration method is chosen for particulate control, it can be demonstrated that the fabric cost is presently less than 1% of the installed filtration system cost. By gaining both particulate and NOx control via conversion to a catalytic fabric, significant economic advantage is gained over the competing high efficiency NOx removal technologies. An economic summary is listed here (2).

	Installed Cost $/KW	Operating Cost mils/kwh
Catalytic Filter Baghouse (650°F System)	178	1-2
Competing High NOx Removal Technologies Adjusted to Include Particulate Control	209-333	11-24

The system modifications required to allow for a high temperature baghouse and installation of the required ammonia injection system are minor compared to the hardware involved with the other competing high NOx removal technologies.

Conclusions

Based upon preliminary, short-term testing, the following conclusions can be made concerning catalytic filter bags.

1. High (>90%) NOx removal can be achieved.

2. Ammonia slip can be kept at low levels.

3. The technology is applicable to different coal types and the subsequent differences in SO_2 levels, ash contents, etc.

4. Cloth and catalyst durability are good.
5. Economics are attractive.

Acknowledgements

The following people were instrumental in the development and advancements made on this project: Stanley J. Miller, Dennis L. Laudal, Greg F. Weber, and Michael L. Jones, all of the Energy and Mineral Research Center at the University of North Dakota; Ken E. Carney and Dennis L. McGarry of Owens-Corning Fiberglas; and Gary M. Nishioka, of H and N Instruments.

References

1. K. E. Carney, OCF communication to EPRI, December 11, 1986.
2. Economics on competing technologies were culled from several EPRI reports. A bibliography is available upon request.

Table 1. PTC Baseline Operating Conditions for First Slipstream Sample Trial

Temperature	650°F
NOx inlet concentration	800 ppm
SO_2 inlet concentration	300 ppm
% O_2	5%
% CO_2	15.5%
Air-to-Cloth ratio	2
NH_3/NOx	1.0
Test duration	11 hours
Coal	Velva, N.D. lignite

Table 2. PTC Baseline Operating Conditions for Second Slipstream Sample Trial

Temperature	650°F
NOx inlet concentration	900 ppm
SO_2 inlet concentration	1600 ppm
% O_2	4.5%
Air-to-Cloth ratio	2
NH_3/NOx	0.9
Test duration	24 hours
Coal	Indiana bituminous

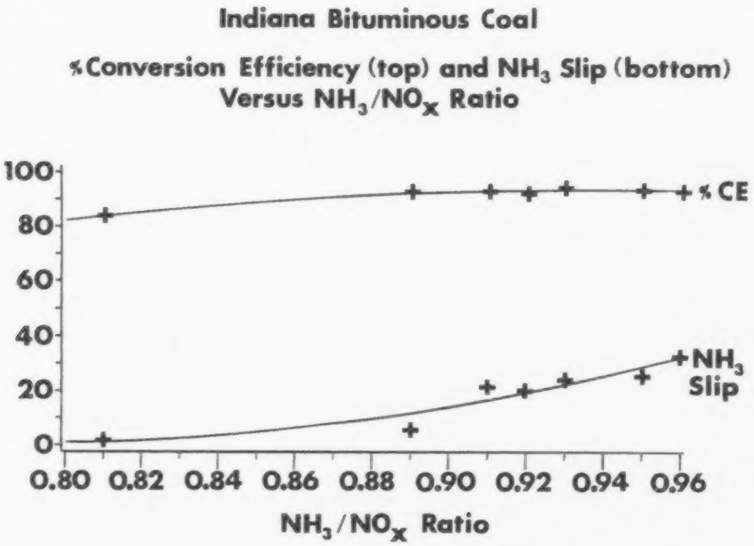


Figure 1

ADVANCED IN-FURNACE NOx CONTROL IN NEW EUROPEAN COAL-FIRED POWER PLANT

Knud Bendixen
Jarl Pedersen
Burmeister & Wain Energi A/S
23 Teknikerbyen
DK-2830 Virum
Denmark

ABSTRACT

NOx-control of coal-fired power plants is a legislative requirement in most communities in the industrialized world. For more than a decade, Burmeister & Wain Energi A/S develops Low-NOx combustion systems, among which some have been installed in power plants in Denmark, Sweden, and in the Federal Republic of Germany, all countries with very strict regulations of the NOx-emissions from coal-fired power plants. In the field of coal combustion in large-scale boilers, BWE has concentrated its developments on tangentially fired boilers having circular Low-NOx burners and supplementary air staging in the furnace.

This paper describes the results obtained during the first 9 months of the operation of the new Low-NOx coal-fired 410 MW_e cogeneration unit No. 9 at Walsum Power Station in the Federal Republic of Germany. The proven NOx-content at furnace outlet is less than 290 ppm (at 3% O_2) at the same time as less than 3% unburned in the fly ash is obtained.

INTRODUCTION

As designer and manufacturer of large-scale boilers, BWE has faced the new requirement of Low-NOx combustion systems caused by the strict regulations of the NOx-emission in Europe, and in compliance with the clients' needs, BWE has developed Low-NOx combustion systems capable of meeting these new standards. To FRG, a country of the world's most strict rules of NOx-emission (Ref. 1), BWE has supplied a new Low-NOx coal-fired cogeneration boiler, Unit No. 9 at Walsum Power Station, mainly used for base-load with a maximum generator rating of 410 MW_e. The performance data are listed in Table 1.

The type of coal used is a domestic medium volatile bituminous coal. The coal analysis is given in Table 2. The general behaviour of the coal is low-reactive, therefore measures must be taken to ensure stable ignition at a burner turn-down ratio of 1:2.5.

The requirement of the NOx-emission at stack outlet is 200 mg/Nm^3 (at 6% O_2, dry gas) corresponding to 120 ppm (at 3% O_2, dry gas), which is attained using a selective catalytic reduction. The requirement of the NOx-emission at furnace outlet is 500 mg/Nm^3 (at 6% O_2, dry gas) corresponding to 290 ppm (at 3% O_2, dry gas) and must be attained within the combustion process.

Preceding page blank

The fly ash must contain no more than 3% unburned carbon, as deposit of fly ash is prohibited in the FRG, and, therefore, it has to be sold as an additive to the cement industry instead.

INSTALLED LOW-NOX COMBUSTION SYSTEM

The boiler is designed for low specific heat release in the furnace, the consequence of which is a furnace volume about twice as big as that of a conventionally designed furnace. At MCR, the specific furnace heat release is 0.105 MW/m^3 (3.71 MW/ft^3), giving a mean residence time of the coal particles of approximately 3.6 sec and a furnace gas outlet temperature of 1210 ^{o}C (2210 ^{o}F).

A tangential firing system with four levels of circular Low-NOx burners was chosen. The air staging Low-NOx combustion system includes six different air streams (Ref. 2).

The relatively low coal reactivity necessitates a fine grinding of the coal:

- max. 20% > 90 microns (170 mesh)
- max. 0.3% > 250 microns (60 mesh)

The coal is pulverized by four vertical roller mills with integrated rotary separators, respectively feeding the four circular Low-NOx burners at the same level.

The distribution of coal and air is within 5% of the mean value. This is achieved for the air flow by separate venturi measurements for each burner, and for the coal flow by using riffle-box coal splitters.

OPERATION AND MAINTENANCE

Ignition stability is strongly promoted by swirl of the secondary air, resulting in a good flame detection and discrimination between individual flames, even at turn-down to 40% burner load. Secondary air swirl has also proven to be favourable as regards minimizing of NOx and unburned in the fly ash.

Tertiary air co-axially around the flame acts as a protecting blanket against corrosion and slag formation, protecting the walls in the nearby burner zone by means of a relatively high O_2-content. The design of the firing system makes it sufficient to operate the sootblowers only once every 24 hours in defiance of the high ash content of the coal, yet providing optimum, reliable performance.

The vertical roller mills were proven capable of grinding the high-ash coal to the required values using a relatively low specific power consumption, 11 kW/t/h.

RESULTS

During the commissioning period various parameter settings for the combustion system were investigated in order to identify the best overall performance:

NOx-content exit furnace	< 290	ppm (at 3% O_2, dry gas)
Unburned in fly ash	< 3	%
CO at furnace walls	< 2000	ppm
O_2 at furnace walls	> 1	%

CO and O_2 were measured locally at a total of 284 locations, resulting in the parameter setting of an air staging in the furnace as shown in Figure 1. This relatively easy parameter setting has proven the NOx-content and unburned in the fly ash to be within the required values with good margins.

As an example of the testing, Figure 2 shows the effect of over-burner air. The feature of the over-burner air is to etablish a relatively fuel-rich Stage 2 of combustion in the centre of the furnace. As can be seen from Figure 2, the NOx-emission is reduced by approximately 50 ppm, corresponding to 15% at full load using over-burner air. Complete combustion and burn-out are established in Stage 3 of combustion, using only 10% over-fire air.

In spite of the difficult type of coal and a newly developed design of the firing system, the take-over by the customer was on schedule.

ACKNOWLEDGEMENTS

The authors wish to thank the following organizations for generously providing equipment and services. The authors also wish to thank the personnel for all services rendered to make this project possible:

- Walsum Power Station
- Steag

REFERENCES

1. O. Rentz and R. Leibfritz. "Overview of Recent Developments in NOx-Control in Europe". Paper presented at the 1987 Joint Symposium on Stationary Combustion NOx Control, march 1987, New Orleans.

2. J. Pedersen. "BWE Low-NOx Combustion Systems". Paper presented at the Swedish Flame Days 1987, September 1987, Studsvik.

The work described in this paper was not funded by the U.S. Environmental Protection Agency and, therefore, the content does not necessarily reflect the views of the Agency, and no official endorsement should be inferred.

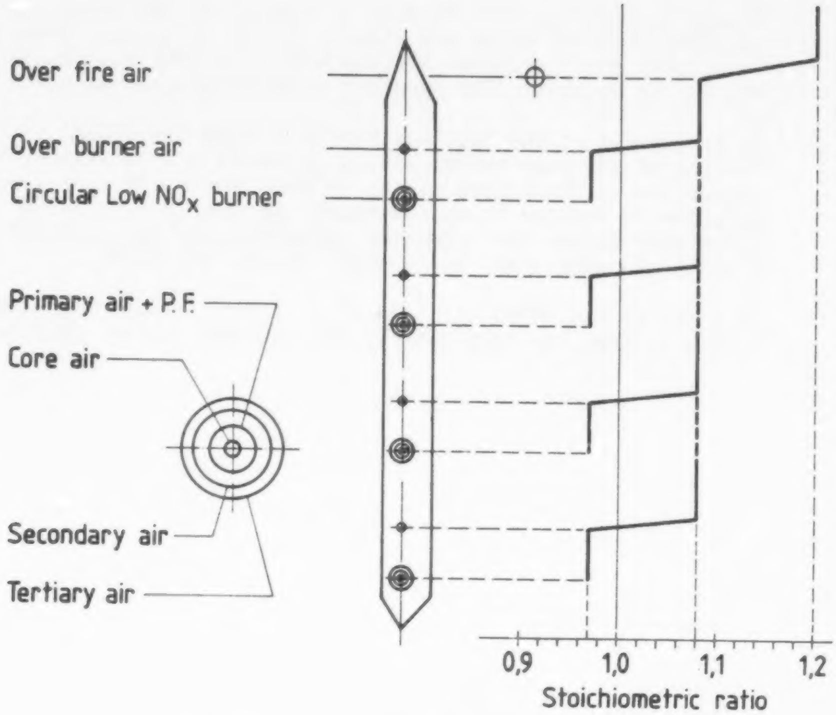


Figure 1. Air Staging Principle

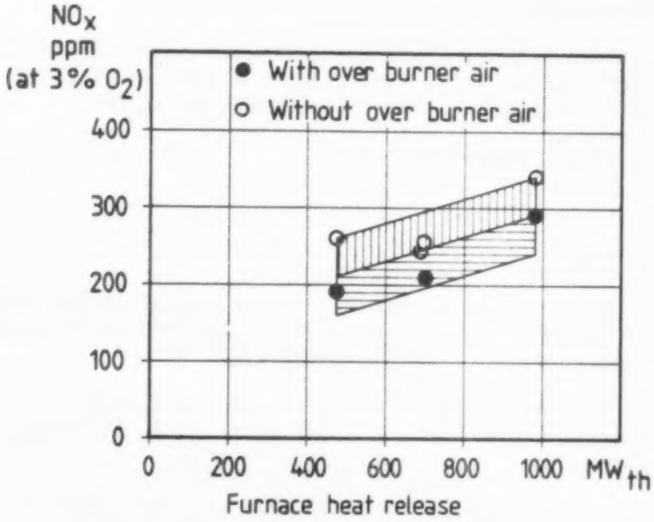


Figure 2. NOx-Content Exit Furnace

Table 1

WALSUM POWER STATION, FRG
Cogeneration Unit No. 9
Performance Data for Coal-Fired Boiler

Steam flow, outlet	335	kg/sec	2,650,000	lb/hr
Steam pressure, outlet	200	bar	2,900	psi
Steam temperature, outlet	535	°C	995	°F
Reheat pressure, outlet	42	bar	610	psi
Reheat temperature, outlet	532	°C	990	°F

Type of Boiler:
- One-pass Benson boiler
- Dry-bottom furnace
- Reheat

Maximum generator rating 410 MW_e

Table 2

WALSUM POWER STATION, FRG
Cogeneration Unit No. 9
Coal Analysis, typical

Proximate, as received:			Ultimate, as received:	
Moisture	8.70	%	Moisture	8.70 %
Ash	24.08	%	Ash	24.08 %
Volatiles	18.69	%	Carbon	57.47 %
Fixed carbon	48.53	%	Hydrogen	3.45 %
			Sulphur	1.04 %
LHV	22.3	MJ/kg	Nitrogen	1.11 %
HHV	10,000	Btu/lb	Oxygen	4.15 %

General behaviour: low reactive

Two-Stage DeNOx Process Test Data from Switzerland's Largest Incineration Plant

by

Dale G. Jones, Ph.D., P.E., EMCOTEK Corporation
Lawrence J. Muzio, Ph.D., Fossil Energy Research Corporation
Erhard Stocker, MHA Basel, City of Basel
Peter C. Nüesch, K+K Ofenbau AG
Stefan Negrea, P.E., KRC Umwelttechnik GmbH
Gert Lautenschlager, Ph.D., Noell GmbH
Erwin Wachter, K+K Ofenbau AG
Gerhard Rose, K+K Ofenbau GmbH

ABSTRACT

A new process for NOx removal using two boiler zones for chemical injection has been installed and tested at KVA Basel, the largest municipal solid waste (MSW) incineration plant in Switzerland. Urea and methanol are used in combination with proprietary injection nozzles to provide NOx removal performance between 65% and 80% at flue gas temperatures varying between 1500 and 1900 F. Methanol is used to provide substantial reduction of ammonia slip and/or air preheater deposits.

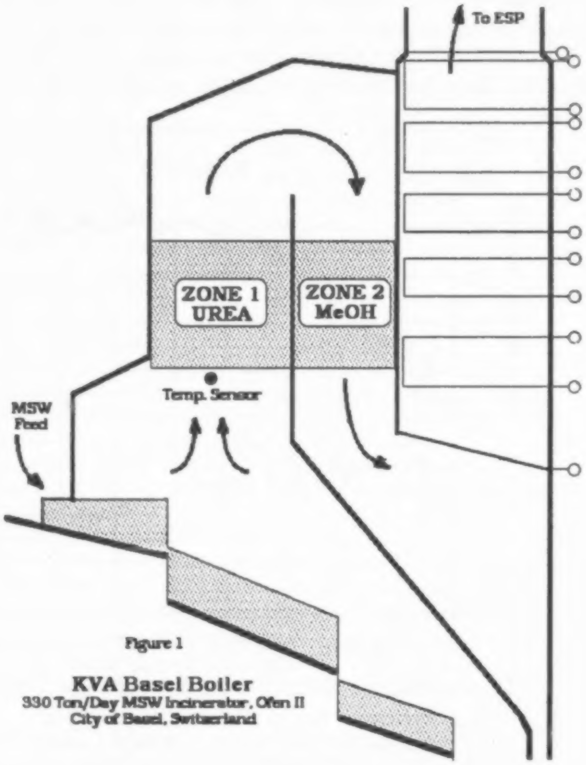


Figure 1

KVA Basel Boiler
330 Ton/Day MSW Incinerator, Ofen II
City of Basel, Switzerland

Preceding page blank

SUMMARY

A new process for NOx removal using two boiler zones for chemical injection has been installed and tested at KVA Basel, the largest municipal solid waste (MSW) incineration plant in Switzerland. Urea and methanol are used in combination with proprietary injection nozzles to provide NOx removal performance between 65% and 80% at flue gas temperatures varying between 1500 and 1900 F. Methanol is used to provide substantial reduction of ammonia slip and/or air preheater deposits. Between 1740 and 1830 F at 65% NOx removal, ammonia slip of 2.5 to 5.0 ppm (without methanol) can be reduced to less than 1.0 ppm. Further commercial development includes award of a contract to install the Two-Stage DeNOx Process on a 325 MW coal-fired boiler in West Germany. The startup date is in August, 1989, and we plan to provide additional details in a forthcoming paper.

PLANT AND DeNOx PROCESS EQUIPMENT DESCRIPTION

There are four boilers at the KVA Basel incineration plant. Two are 46 years old (each rated at 220 TPD) and two are 24 years old (each rated at 330 TPD). The Two-Stage DeNOx Process was installed on one of the larger boilers. Figure 1 provides a furnace system cross-section which shows the two zones of chemical injection, the flue gas flow path, and the location of the temperature sensor used for process control. Urea is provided in bulk granular form and mixed with water prior to being pumped to proprietary injection nozzles in the first zone. Methanol (or MeOH) is supplied by liquid pumps to the second-zone injector nozzles. The flowrates of chemical(s) to the various injection locations are controlled by the single flue gas temperature sensor. The flue gas flowrate is 52,000 DSCFM at 11% O2 and the uncontrolled NOx level is 160 dppm. To provide a high degree of flue gas mixing, injector system airflow totalling 1500 SCFM is used.

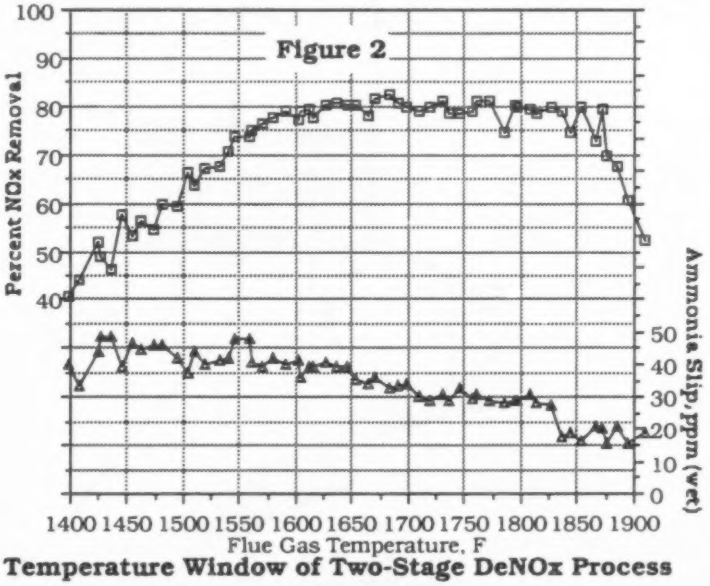


Figure 2

Temperature Window of Two-Stage DeNOx Process

Total Injection System Airflow = 1500 SCFM
Molar Ratios: (Urea/NOx) = 0.80 and (MeOH/NOx) = 0.14
Initial NOx = 160 dppm & Flue Gas Flow = 52,000 DSCFM (11% O2)

WIDTH OF THE TEMPERATURE WINDOW

Due to wide variations in burning characteristics of the solid waste, the flue gas temperature (measured by thermocouple upstream from the first injection zone) varies between about 1400 and 1900 F. The control system compensates for much of this temperature fluctuation by changing the location(s) at which chemical(s) are injected. As shown in Figure 2, using a molar ratio of urea/NOx of 0.80 plus methanol/NOx of 0.14 produces 80% NOx removal in the KVA Basel boiler at flue gas temperatures between 1600 and 1850 F. The data in Figure 2 was collected at 5-second intervals and subsequently averaged for a 24-hr period of operation. Scatter in the averaged values are due to rapid temperature fluctuations in the KVA Basel furnace. The wide temperature window for high levels of DeNOx is due to (a) a high degree of flue gas mixing provided by proprietary injector nozzles, (b) operation of the temperature control system to adjust the location(s) where chemical(s) are injected, and (c) the drying time for urea droplets, which provides some delay and allows better urea dispersion before DeNOx reactions begin to occur. We have called this delay time phenomenon the "popcorn effect".

UREA/NOx MOLAR RATIO

Figure 3 shows the effect of urea/NOx molar ratio on percent NOx removal. DeNOx levels of 78%, 65%, and 48% are achieved at urea/NOx molar ratios of 0.80, 0.60, and 0.40, respectively. The corresponding percentages of urea utilization are 49%, 54%, and 60%. By definition, a urea/NOx molar ratio of 0.50 equals 1.0 moles of NH2 per mole of NOx. These results are believed to be representative for electric utility boilers where the flue gas temperature at any given injection location can be maintained in a desired range from about 1740 to 1830 F.

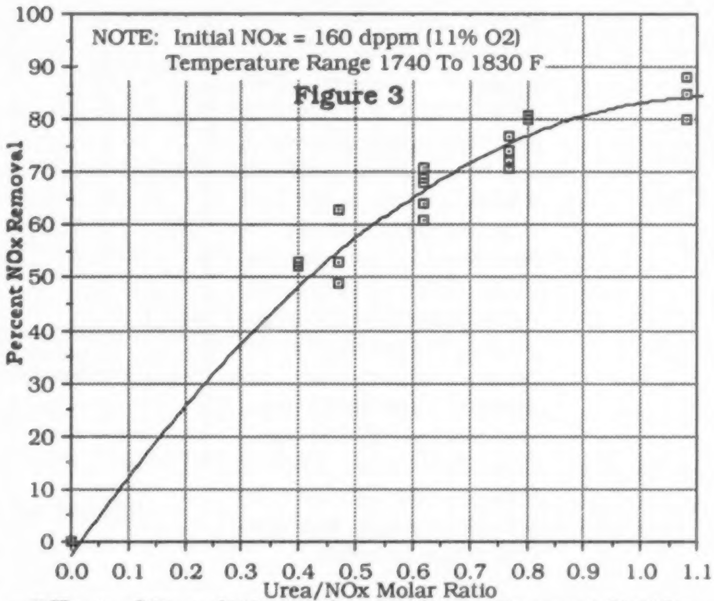


Figure 3

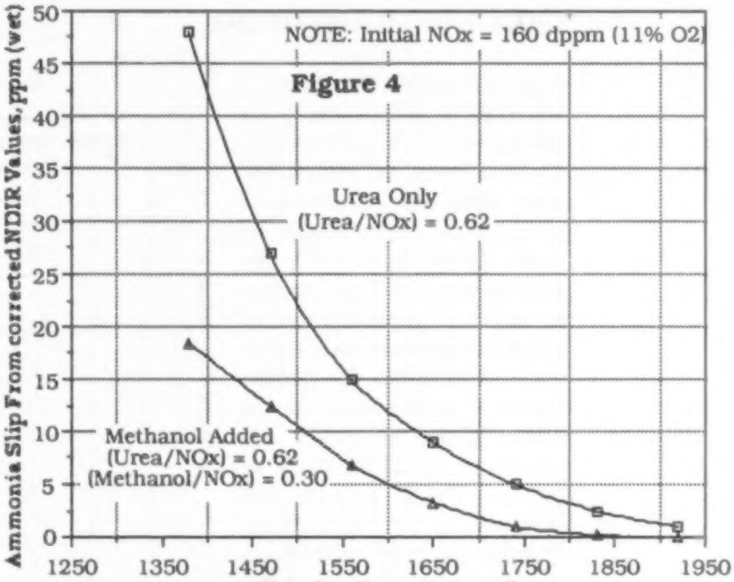
Effect of Urea/NOx Molar Ratio on Percent DeNOx

DATA ACQUISITION

Extreme care was taken to obtain repeatable and representative data during a two-month testing program. For example, NO signals were obtained using two separate gas analyzers: one chemiluminescent type and one NDIR type. In the same way, duplicate signals were obtained for O2 and CO, and all signals, including boiler and process operating parameters, were recorded using a computerized data-logging system. Ammonia slip values were also determined by two different methods: (a) continuous NDIR gas analyzer (operating at 500 F), and (b) 15-minute grab samples analyzed by wet chemistry. It was found that both methods of ammonia sampling provided consistent and representative results.

AMMONIA SLIP REDUCTION USING METHANOL

One of the important features of the Two-Stage DeNOx Process is the use of methanol to reduce ammonia slip and related concerns including air-preheater deposits. At KVA Basel, relatively high levels of ammonia slip (i.e. 15 to 40 ppm at urea/NOx ratio of 0.80) can be tolerated since the ESP system operates at 460 F and there is very little deposition of ammonia salts, either on equipment surfaces or ESP ash. For coal-fired boiler applications, however, such high levels of ammonia slip are unacceptable. Figure 4 shows ammonia slip as a function of flue gas temperature, both with and without methanol injection at a urea/NOx ratio of 0.62, corresponding to 65% NOx removal. As can be seen, when methanol is added, very large reductions in ammonia slip are realized. Between 1740 and 1830 F at 65% NOx removal, ammonia slip of 2.5 to 5.0 ppm (without methanol) can be reduced to less than 1.0 ppm. In coal-fired boiler applications, this would be critically important for minimizing air preheater deposits and/or, when required, ammonia contamination of ESP ash. The Two-Stage DeNOx Process can thus be optimized to meet site-specific requirements.

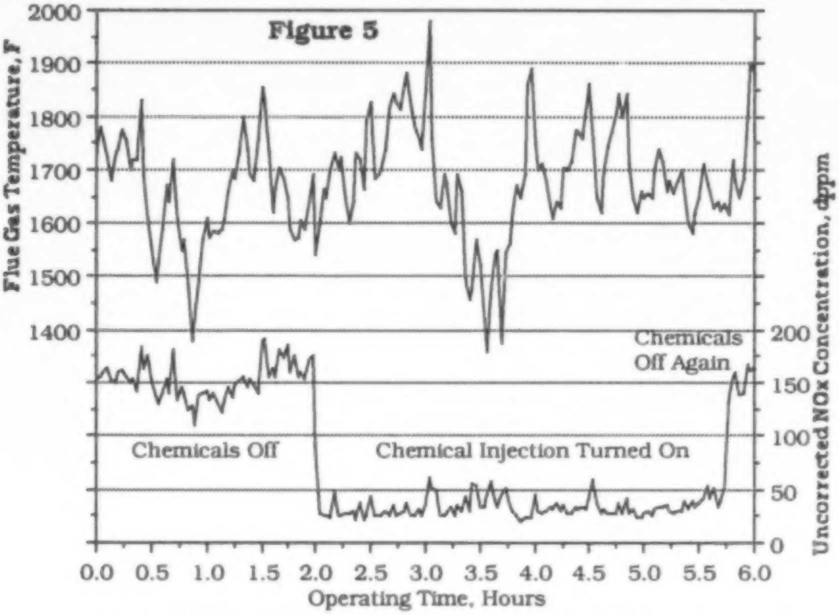


Effect of Methanol Injection on NH3 Slip

OPERATIONAL CHARACTERISTICS AND DISCUSSION

Despite rapid flue gas temperature fluctuations of up to 100 F per minute observed at KVA Basel, the Two-Stage DeNOx Process provides relatively uniform, reduced levels of outlet NOx concentration. In Figure 5, typical strip chart records of gas analyzer NOx signals show variations from 150 ± 40 ppm (without chemical injection) to 40 ± 20 ppm (with chemical injection).

The 160 dppm initial NOx level at KVA Basel is relatively low. At higher NOx levels, the percentage NOx reduction increases for a given urea/NOx molar ratio. In higher NOx



Operating Characteristics From Chart Records

level applications, the Two-Stage DeNOx Process is expected to operate with (a) lower urea ratio, and/or (b) reduced injector system flowrate at a given DeNOx performance level. It should also be noted from Figures 2, 3, & 4 that ammonia slip increases sharply when DeNOx is increased above about 65%. Whether or not this is an unavoidable consequence of fundamental NHi-radical chemistry remains an open question.

In the KVA Basel boiler, there is a relatively high degree of stratified flue gas flow which requires that high levels of chemical mixing be provided by the injection system. This is why the injector airflow requirement is as high as about 3% of the total flue gas mass flowrate. Typical electric utility boilers have a much higher level of natural turbulence, so that the injector system flow requirement is less. For example, typical designs for utility boilers show that the Two-Stage DeNOx Process achieves performance levels similar to those observed at KVA Basel with an injector system flow requirement between only 0.6% and 1.0% of the flue gas mass flowrate.

Proprietary injector nozzles are an important part of the Two-Stage DeNOx Process. Boiler flow models and computer simulations are used to optimize the design of specific injection systems. The Two-Stage DeNOx Process is based on simple engineering principles which are applied to specific boiler configurations using sophistocated design techniques. Proprietary chemicals are not used.

Further commercial development includes award of a contract to install the Two-Stage DeNOx Process on a 325 MW coal-fired boiler in West Germany. The startup date is in August, 1989, and we plan to provide additional details in a forthcoming paper.

EFFECTS OF CATALYST DEVELOPMENTS OF THE ECONOMICS OF SELECTIVE CATALYTIC REDUCTION

T. R. Gouker, J. P. Solar, and C. P. Brundrett*
W. R. Grace & Co.-Conn., Research Division
7379 Route 32
Columbia, Maryland 21044

ABSTRACT

This paper reports a quantitative analysis of the economics of SCR based on recent commercial developments in West Germany. The costs of selective catalytic reduction (SCR) have dropped significantly since the technology was introduced in Japan in the 1970's. The drop in SCR cost is shown to result from catalyst price reductions, increases in catalyst lifetime, and improvements in catalyst activity. This analysis suggests that any further significant cost reduction will have to come from improvement in catalyst activity. A Grace proprietary formulation which has a 50% increase in activity, resulting in a 20% decrease in both operating and capital costs, will be described.

INTRODUCTION

Selective catalytic reduction (SCR) is now widely used for the removal of nitrogen oxides from power plant stack gases in both Japan and West Germany and is a leading candidate technology to meet potential future emission standards in the U.S. The costs of implementing this control technology have been decreasing steadily since SCR was first commercialized in the 1970's and costs have been significantly reduced in the 1980's. Both catalyst price and installation cost have dropped during the installation of SCR facilities in West Germany. In addition, improvements in catalyst activity have occurred, leading to additional reductions in both capital and operating costs. Since the economics of SCR have not been addressed in the U.S. since the early 1980's[1], it is appropriate to reevaluate the economics of SCR prior to its possible introduction in the U.S.

Process costs are shown to be highly sensitive to both catalyst cost and performance. Factors evaluated include reductions in catalyst price, improvements in catalyst activity, and increases in the useful lifetime of the catalyst. When combined, these factors have decreased the current estimated operating cost of SCR by 50% over the levels anticipated when legislation was enacted in West Germany. In addition, this analysis suggests that research on additional improvements in catalyst activity, rather than reductions in price alone, offers the largest potential opportunity to further impact SCR economics. Grace has identified a proprietary catalyst formulation which has 50% higher activity. It has been calculated to decrease both the capital and operating costs of SCR by 20%.

---

* W.R. Grace and Co.-Conn., Davison Chemical Division
10 East Baltimore Street
Baltimore, Maryland 21202

Preceding page blank

BASE CASE

As a basis for comparative evaluation, the West German experience in SCR retrofitting has been summarized and reflected for the case of a 500 MW, coal-fired power plant. The boiler in this case has first been retrofit with a low NO_x burner at a cost of 0.06 Pf/kWh. Thus, at an uncontrolled NO_x emission level of 1100 mg/m^3 (535 ppm), a low NO_x burner reduces emissions to roughly 800 mg/m^3 (390 ppm). Installation of SCR at an 80% removal efficiency results in a final NO_x level of 160 mg/m^3 (78 ppm), which is below the regulated level of 200 mg/m^3 (97 ppm). For the cases considered in this paper, the SCR unit is located in the high-dust position under typical commercial conditions. At a flue gas flow rate of 1.55 mm Nm^3/hr, a temperature of 380°C, and a sulfur concentration of 2000 mg/m^3 (700 ppm), ammonia slip is limited to 5 ppm. The catalyst used in the base case is a titania-based 7.4 pitch honeycomb representative of those used in current West German installations.

The base case, shown in the table, thus describes the averaged costs for installation and operation of such a facility in West Germany. Although catalyst prices of 45,000 DM/m^3 were common in the early 1980's when West German utility companies first considered SCR installations, an average price based on recent sales of 25,000 DM/m^3 has been used in this case. In addition, the current catalyst replacement strategy has been incorporated, resulting in an average catalyst life of four years. The capital investment of 55 Mio DM and operating costs of 0.56 Pf/kWh are consistent with other studies of West German installations[2,3].

CATALYST COST

The most significant impact on SCR economics during its introduction in West Germany has been the large reduction in catalyst price. As shown in Figure 1, the 45% reduction experienced in catalyst price between 1984 and 1988 has led to about a 25% reduction in the cost of operating an SCR facility. For a facility installed today, there would be a corresponding reduction in capital costs for the initial catalyst charge. The dramatic decrease in catalyst price can be attributed to two factors: replacement of high-price Japanese suppliers with modern, efficient manufacturing plants in Europe, and the formation of a competitive market. The competitive market was driven by an over-supply of production capacity in the early years of the West German market. It is not yet clear whether the current price of 25,000 DM/m^3 used in the base case is at market equilibrium or whether the catalyst producers can operate profitably at this level. However, further reductions in price are unlikely due to the inherent raw materials and manufacturing costs of the current titania-based catalysts in commercial use. Even if additional reductions were possible, the impact of further price drops is diminished relative to what has already occurred. Figure 1 shows that an additional 10% cut to 22,500 DM/m^3 results in a savings of 4% in total operating cost.

CATALYST LIFE

Significant extension of the average catalyst life, which acts to reduce SCR operating cost, has also occurred during the 1980's. Early assumptions of a two year catalyst life have been increased to three or four years based on experience in Japan. At a guarantee of three years of acceptable activity, innovations in catalyst replacement strategy, through a staged replacement schedule of one layer of the reactor inventory annually, allow for an average catalyst life of at least four years. Figure 2 shows the cost impact of the catalyst life out to eight years. Compared to the base case of four years, an average life of two years had a 38% higher operating cost. Further life extensions through six to eight years, however, provide a diminishing return.

CATALYST ACTIVITY

The third factor affecting the cost of SCR, catalyst activity, has received a great deal of attention due to the reduction in installed catalyst volume possible with increased activity. Reduction of catalyst volume not only reduces operating costs, but also capital requirements due, for example, to the use of a smaller reactor and I.D. fan along with less catalyst. A number of improvements have been identified recently and their impact on costs is shown in the cases presented in Figure 3. Two approaches have been taken to increase the activity of a given reactor volume: incorporation of higher geometric surface area, and improvement of catalytic performance within the walls of the catalyst. Increased geometric surface area has been obtained by reducing the pitch of the honeycomb from 7.4 to 6.7. This increases the number of channels from 400 to 484 within each element. To prevent dust plugging, the catalyst wall thickness has been reduced from 1.4 mm to 1.0 mm. This change in catalyst pitch has resulted in a 10% reduction in both capital and operating cost.

Improving the performance of catalytic materials also results in volume reductions for an SCR reactor. Research has shown that, due to gas diffusion limitations, only the ca. 100 microns nearest the catalyst surface are utilized in the current catalysts. Through pore structure optimization, access to the catalyst interior can be made more effective without reducing the number of catalytically active sites[4]. Catalyst formulations with a 15% improvement in activity are being demonstrated in West German pilot plants and Grace has identified formulations which increase catalyst activity by 50% over the technology used in the base case. These improvements translate into a 13% and 33% reductions, respectively, in required catalyst volumes. As can be seen in Figure 3, activity improvement of up to 50% result in additional reductions of 20% in both capital and operating cost. The 50% activity improvement of Grace's new catalyst formulation also provides the potential for further increases in catalyst life, providing for an additional savings in operating cost.

ACKNOWLEDGEMENTS

The authors would like to acknowledge the assistance of Professor Otto Rentz for his help in obtaining references to the West German SCR experience.

REFERENCES

[1] Bauer, T.K., et al. Selective Catalytic Reduction for Coal-Fired Power Plants: Feasibility and Economics. Stearns-Roger Engineering Corporation, Denver, Colorado. EPRI CS-3603, October, 1984.

[2] Schönbucher, B. "Costs of a DENOX Plant on the Basis of the SCR Process." Proceedings of the Workshop on Emission Control Costs. Ed. O. Rentz, et. al. Karlsruhe: Institute for Industrial Production, University of Karlsruhe, 1987, pp. 279-296.

[3] Schärer, B., et al. "Costs of Retrofitting Denitrification." Proceedings of the Workshop on Emission Control Costs. Ed. O. Rentz, et. al. Karlsruhe: Institute for Industrial Production, University of Karlsruhe, 1987, pp. 326-358.

[4] Beeckman, J.W. and Hegedus, L.L. "Design of Monolith Catalysts for Power Plant NO_x Emission Control." Proceedings of the 1988 Annual Meeting of the American Institute of Chemical Engineers. Washington, D.C., December 1988, 72e.

FIGURE 1

Effect of Catalyst Price

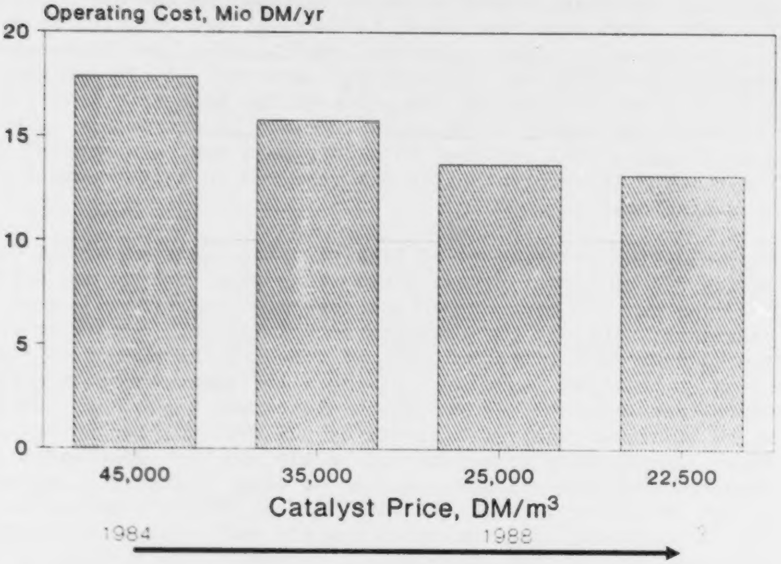


FIGURE 2

Effect of Catalyst Life

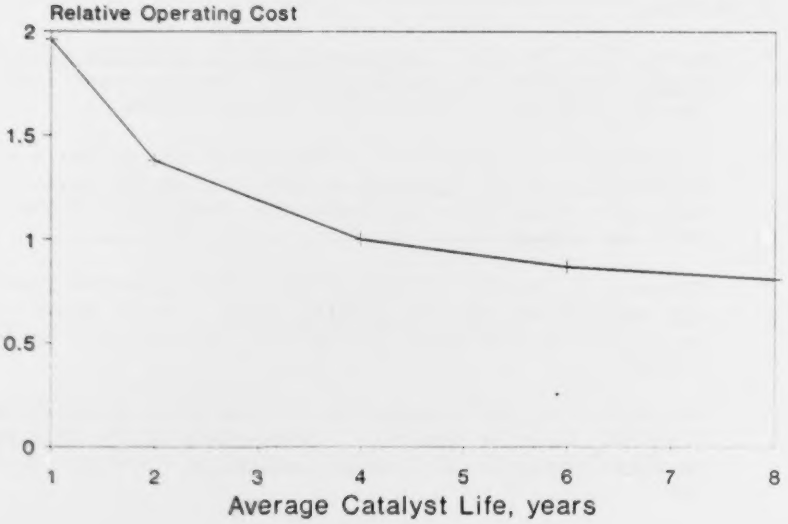


FIGURE 3

Effect of Catalyst Improvements

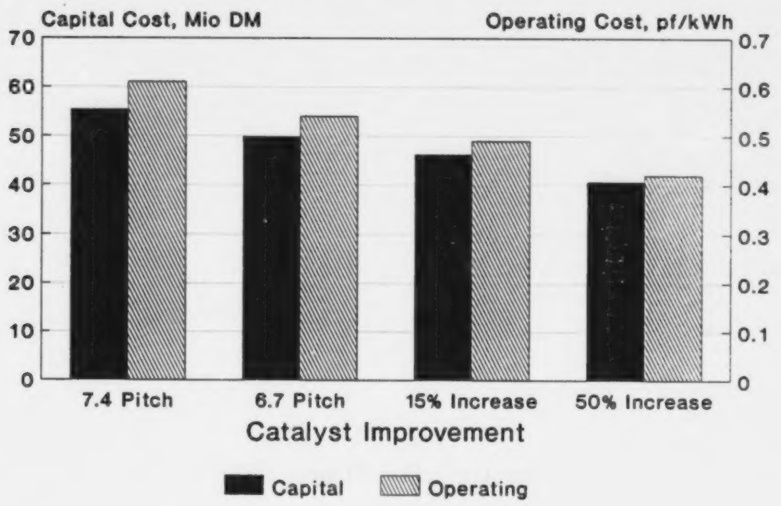


TABLE 1

SUMMARY OF BASE CASE COSTS

Capital Investment Mio DM	
Catalyst	15.6
Reactor/Controls	15.2
Ammonia System	4.0
Duct Work/Dampers/ I.D. Fan	4.6
Air Preheater	2.1
Site and Steel Work	5.8
Electrical	1.6
Subtotal	48.9
General Facilities	1.9
Engineering	2.2
Construction Interest	2.4
Total Capital	55.4

Operating Costs Mio DM/yr	
Variable Operating Costs	
Catalyst	5.21
Ammonia	0.66
Power/Steam	1.05
Subtotal	6.91
Fixed Operating Costs	
Operating labor	0.37
Maintenance - Material and labor	1.12
Administration/Tax/ Insurance	0.97
Subtotal	2.46
Capital Servicing	
Depreciation	2.80
Interest	1.50
Subtotal	4.30
Total Operating Cost	13.67

FULL SCALE DEMONSTRATION OF ADDITIVE NO_2 REDUCTION(1) WITH DRY SODIUM DESULFURIZATION

Verle V. Bland
KVB, Inc.
Denver, Colorado 80226

ABSTRACT

Recent work in the area of dry sodium injection for flue gas desulfurization, has underscored the effectiveness of this technology for use in low-sulfur coal applications in the power industry. Dry sodium injection, however, results in increased concentrations of NO_2 in the flue gas exiting the scrubbing process. Higher NO_2 concentrations at the stack can result in an undesirable brown plume coloration which could considerably reduce the desirability of the technology to potential users.

Several additive compounds successful in controlling NO_2 formation from sodium injection, have been identified in the laboratory and evaluated in a fabric filter pilot plant system. This paper reports results of full scale testing of three such additive compounds (urea, anhydrous ammonia, and ammonium bicarbonate) at the City of Colorado Springs R.D. Nixon Generating Station Dry Sodium Injection Demonstration Facility.

INTRODUCTION

In Phase 1 of the Sodium Injection Project at the R. D. Nixon Power Plant (completed in April, 1986), dry injection of sodium compounds into the flue gas stream prior to the fabric filter, was shown to be an effective and economical SO_2 removal technique. Only one major problem was revealed during the test work, namely, the appearance (at the stack exit) of a faint reddish-brown plume whenever the SO_2 control level exceeded 50%. At the time, it was theorized that the cause of the visible plume was increased NO_2 emissions resulting from the dry sodium desulfurization process.

This phenomenon had been previously observed during related EPRI research at the Arapahoe pilot plant test facility. This research, conducted by KVB, had identified several additive compounds that exhibited a high potential for successfully controlling this NO_2 emissions problem. Therefore, the purpose of Phase 2 of the R. D. Nixon Sodium Injection Demonstration Project was to further evaluate the use of these NO_2 reducing additives on a full scale fabric filter installation.

Preceding page blank

PROCESS DESCRIPTION

In the sodium desulfurization process, sodium bearing crystalline compounds (normally bicarbonate or sesquicarbonate) are pulverized and injected directly into a coal combustion flue gas. Once the sorbent enters the gas stream, SO_2 diffuses to the particle surface where it reacts to form sodium sulfate.

Lower NO_x emissions also result from the dry injection of sodium compounds. The mechanism by which this occurs is not well understood, but the demonstrated capability of this process to reduce NO_x levels could be significant. One serious side-effect, however, does result from this NO_x reduction. This side-effect is an increase in NO_2 emissions across the dry scrubbing process; and since NO_2 is a reddish-brown gas, its presence can create an undesirable coloration to the power plant exhaust plume.

During previous pilot scale EPRI research, a number of additives were identified as possessing potential in reducing this plume coloration problem. These additives were:

- anhydrous ammonia (NH_3)
- ammonium bicarbonate (NH_4HCO_3)
- urea (NH_2CONH_2)

Anhydrous ammonia appeared to aid in solution of the problem by reacting directly with NO_2 in the gas stream, and, although not previously evaluated for this purpose, it was assumed that ammonium bicarbonate would act in somewhat the same manner. Urea, however, appeared to work not only by releasing ammonia to react directly with NO_2, but by inhibiting the actual process that produces NO_2 in the first place. While the mechanisms are still not well understood and further evaluation would be desirable, the Arapahoe results provided the incentive to evaluate these compounds at the full scale.

SYSTEMS DESCRIPTION

The host facility for this demonstration was Unit No. 1 of the City of Colorado Springs Ray D. Nixon power plant. The facility is a 222-MW pulverized, low-sulfur coal unit employing two parallel fabric filter baghouses for particulate control.

The sodium injection system has a 100+ MW capability for treating flue gases entering one of the two baghouses. The remaining baghouse flue gas was untreated and as such served to provide valuable baseline information during the test project.

Two NO_2 control additive injection systems were installed at the Nixon plant. One system supplied superheated ammonia vapor to the sodium desulfurization process; the other system supplied either urea or ammonium bicarbonate as a pulverized solid.

NO_2 REDUCTION ADDITIVE EVALUATION

Baseline tests were first completed with both sodium sesquicarbonate and sodium bicarbonate to establish NO_2 emission levels (Figure 1). Then, tests with the three additive compounds (urea, ammonia, and ammonium bicarbonate) were conducted over a range of additive feed rates, sorbent feed rates, and flue gas temperatures. Although variable, nominal conditions for the majority of these tests were:

flue gas temperature = 280°F
inlet SO_2 @ 3% O_2 = 400 ppm
inlet NO @ 3% O_2 = 350 ppm
sodium sesquicarbonate NSR = 1.5
sodium bicarbonate NSR = 0.9

To establish performance curves, additive feed rates ranging from 1 to 20 percent by weight of the injected sodium sorbent were evaluated. Figures 2 and 3 show these results. The maximum feed rate tested was different for each additive. For urea, 100% NO_2 removal was attained at feed rates from 11 to 12 percent, making additional injection unnecessary. For NH_3, the maximum addition rate was 10% (75% NO_2 removal) due to a vaporizer system limitation. However, only a marginal increase in NO_2 removal was experienced by increasing the ammonia addition rate from 7 to 10 percent, indicating higher rates may not have resulted in additional NO_2 reduction. Finally, the maximum ammonium bicarbonate (ABC) rate of 20% was dictated by mechanical throughput limitations of the dry additive feed system. NO_2 removal of only 41% was observed for ABC at this maximum feed rate.

Since an NO_2 concentration of approximately 30 ppm was identified as the visual threshold from the R. D. Nixon stack, reducing emissions below this level was desirable. The visual threshold for NO_2, at other locations, would depend on a number of factors and thus is site-specific. For SO_2 removals ranging from 70 to 90 pecent, the dry sodium scrubbing process resulted in an outlet NO_2 concentration averaging 50 ppm. To be safely below the visual threshold, a reduction in NO_2 of approximately 50% was required. The data in Figures 2 and 3 show that urea and ammonia were about equally effective in attaining this goal. An addition rate of approximately 3.5% of either compound resulted in 50% NO_2 removal. ABC, however, was not as effective. An ABC addition rate of 3.5% only resulted in a 10% reduction of the NO_2 emissions.

Overall system NO_x emissions were also affected by additive injection. NO_x removal typically, but not always, increased with the use of each additive. Figure 4 shows comparable data for urea, ammonia, and ABC injection. For these tests, an increase in NO_x removal from 3 to 30% was observed.

CONCLUSIONS

This project demonstrated, on a full scale utility boiler, that the use of additives can successfully eliminate the brown plume problem associated with dry sodium injection. An addition rate of approximately 3.5% (lb additive/lb sorbent) of either urea or ammonia reduced the NO_2 from 50 ppm to 25 ppm (below the visual threshold for the Nixon plant). Ammonium bicarbonate, however, was not very effective. A 3.5% additive injection rate resulted in only 10% NO_2 removal.

REFERENCE (1):
Bland, V. V., KVB, Inc., J. J. Hammond, Colorado Springs Dept. of Utilities, R. G. Rhudy, EPRI, "Full Scale Demonstration of Additive NO_2 Reduction with Dry Sodium Desulfurization," presented at First Combined FGD and Dry SO_2 Control Symposium, Cosponsored by EPA and EPRI, October 25-28, 1988, St. Louis, MO.

NO_2 REDUCTION ADDITIVE EVALUATION

Baseline tests were first completed with both sodium sesquicarbonate and sodium bicarbonate to establish NO_2 emission levels (Figure 1). Then, tests with the three additive compounds (urea, ammonia, and ammonium bicarbonate) were conducted over a range of additive feed rates, sorbent feed rates, and flue gas temperatures. Although variable, nominal conditions for the majority of these tests were:

flue gas temperature = 280°F
inlet SO_2 @ 3% O_2 = 400 ppm
inlet NO @ 3% O_2 = 350 ppm
sodium sesquicarbonate NSR = 1.5
sodium bicarbonate NSR = 0.9

To establish performance curves, additive feed rates ranging from 1 to 20 percent by weight of the injected sodium sorbent were evaluated. Figures 2 and 3 show these results. The maximum feed rate tested was different for each additive. For urea, 100% NO_2 removal was attained at feed rates from 11 to 12 percent, making additional injection unnecessary. For NH_3, the maximum addition rate was 10% (75% NO_2 removal) due to a vaporizer system limitation. However, only a marginal increase in NO_2 removal was experienced by increasing the ammonia addition rate from 7 to 10 percent, indicating higher rates may not have resulted in additional NO_2 reduction. Finally, the maximum ammonium bicarbonate (ABC) rate of 20% was dictated by mechanical throughput limitations of the dry additive feed system. NO_2 removal of only 41% was observed for ABC at this maximum feed rate.

Since an NO_2 concentration of approximately 30 ppm was identified as the visual threshold from the R. D. Nixon stack, reducing emissions below this level was desirable. The visual threshold for NO_2, at other locations, would depend on a number of factors and thus is site-specific. For SO_2 removals ranging from 70 to 90 pecent, the dry sodium scrubbing process resulted in an outlet NO_2 concentration averaging 50 ppm. To be safely below the visual threshold, a reduction in NO_2 of approximately 50% was required. The data in Figures 2 and 3 show that urea and ammonia were about equally effective in attaining this goal. An addition rate of approximately 3.5% of either compound resulted in 50% NO_2 removal. ABC, however, was not as effective. An ABC addition rate of 3.5% only resulted in a 10% reduction of the NO_2 emissions.

Overall system NO_x emissions were also affected by additive injection. NO_x removal typically, but not always, increased with the use of each additive. Figure 4 shows comparable data for urea, ammonia, and ABC injection. For these tests, an increase in NO_x removal from 3 to 30% was observed.

CONCLUSIONS

This project demonstrated, on a full scale utility boiler, that the use of additives can successfully eliminate the brown plume problem associated with dry sodium injection. An addition rate of approximately 3.5% (lb additive/lb sorbent) of either urea or ammonia reduced the NO_2 from 50 ppm to 25 ppm (below the visual threshold for the Nixon plant). Ammonium bicarbonate, however, was not very effective. A 3.5% additive injection rate resulted in only 10% NO_2 removal.

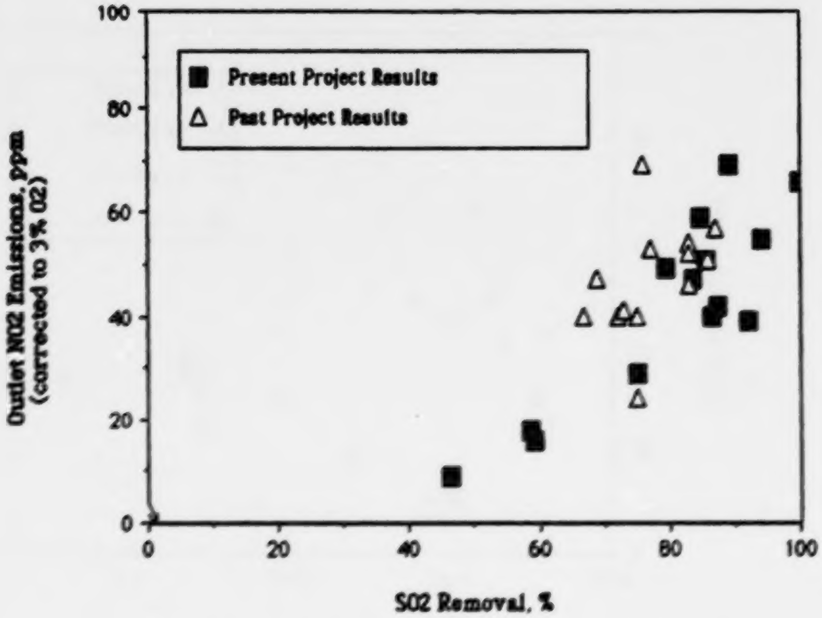


Figure 1. Comparison of Phase 1 and Phase 2 Outlet NO2 Emissions Versus SO2 Removal for Sodium Sesquicarbonate Injection.

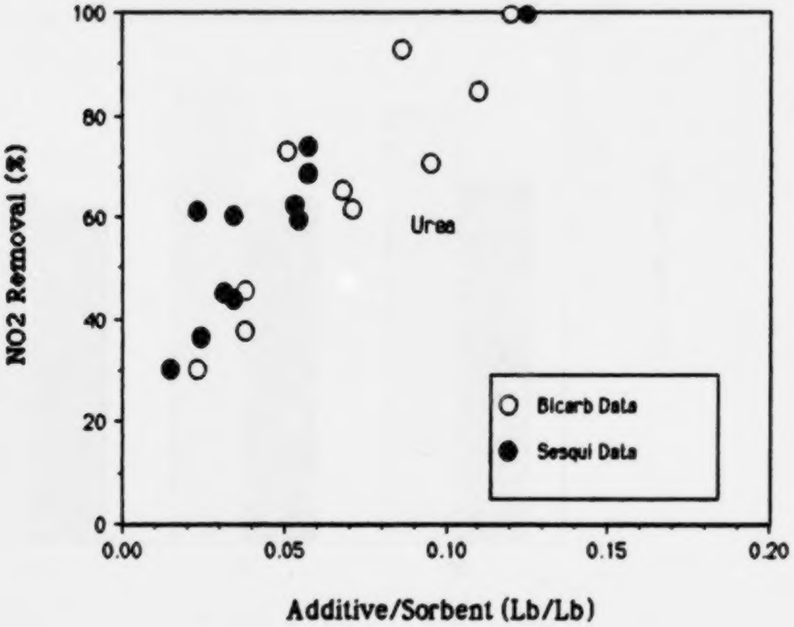


Figure 2. NO2 removal as a function of additive to sorbent mass ratio for urea.

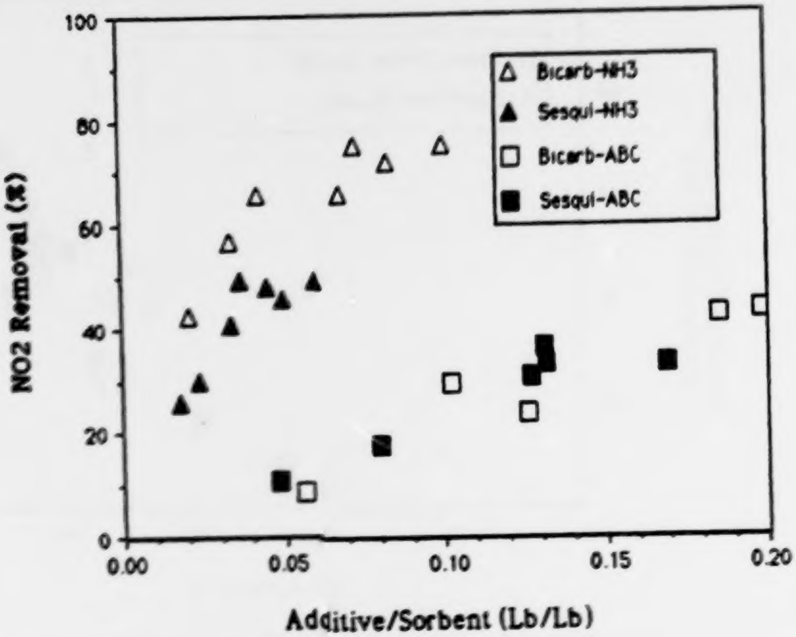


Figure 3. NO2 removal as a function of additive to sorbent ratio for NH3 and ABC

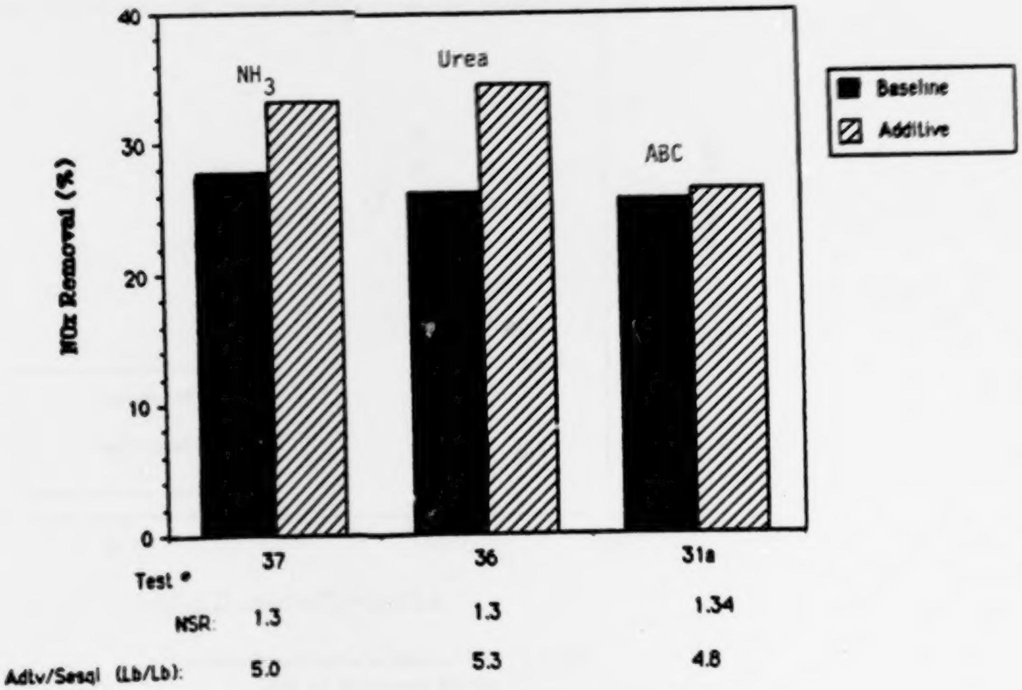


Figure 4. Effects of additive use on NOx removal

SHELL PROCESS FOR LOW-TEMPERATURE NO_x CONTROL

Frans Goudriaan and Carl M.A.M. Mesters*
Koninklijke/Shell-Laboratorium, Amsterdam
(Shell Research B.V.)
Badhuisweg 3, 1031 CM Amsterdam, The Netherlands

and

René Samson
Shell Internationale Chemie Maatschappij B.V.
The Hague, The Netherlands

ABSTRACT

This paper describes a process developed by Shell for the selective catalytic reduction of nitrogen oxides.
A vanadium/titanium-on-silica catalyst has been developed for this process. The stability of the catalyst is excellent.
The high catalyst activity allows operation at temperatures as low as 130 to 200 °C. The lower temperature limit is determined by the amount of sulphur dioxide the flue gas.
To minimise pressure drop and to permit operation with dust-containing flue gases improved version of the Parallel Passage Reactor has been developed.
Several commercial projects are under way.

INTRODUCTION

NO_x emission must be reduced drastically in the years to come, as an essential contribution to a cleaner environment. In both the USA and Europe the legislation on NO_x levels in flue gases from stationary installations is tending to become more restrictive. In most cases, primary reduction methods such as the use of low-NO_x burners will not in future suffice. Increasingly, therefore, it will be necessary to adopt secondary methods, such as Selective Catalytic Reduction (SCR) with ammonia.

This paper gives the status of the Shell SCR process for low-temperature deNOxing.

CATALYST: LABORATORY WORK

At the heart of the Shell SCR process is a highly active and selective catalyst. In a previous publication (1) the development of an optimally impregnated vanadium/titanium-on-silica catalyst has been described. The carrier is Shell silica with a surface area of 300 m^2/g and a pore volume of 0.9 ml/g. It is shaped either as spheres (S-995) or as granules (S-095), the size of which is adapted to the application concerned.

---

* Presently with Shell Development Co., Houston, Texas, USA.

Further development has resulted in a patented catalyst which is easier to manufacture and has a higher stability, whilst the high activity is maintained. The effect of the vanadium and titanium load is shown in Figure 1. The deNOxing activity here is given as the percentage NO_x conversion in a simple laboratory catalyst ranking test, details of which are given in Table 1. Figure 1 shows clearly the combined effects of titanium and vanadium content. At a constant V load the activity can be greatly increased by increasing the Ti load and vice versa.

An in-depth study of the structure of the catalyst has enabled us to pinpoint the essential features of an active V-Ti/SiO_2 deNOxing catalyst:
* Both Ti and V are very highly dispersed, as evidenced by XRD/SEM/TEM. Almost no crystalline V_2O_5 or TiO_2 (anatase or rutile) are present.
* Both Ti and V are intimately mixed with SiO_2 (XPS analysis).
* Part of the Ti is present in a four-fold coordination with oxygen (i.e., not six-fold as in anatase or rutile).
* Part of the V is present as V^{4+}. These species are stabilised by titanium.
* The resulting surface area of the catalyst is relatively high (150 - 250 m^2/g)

CATALYST PERFORMANCE IN FLUE GAS

A laboratory study has been conducted with S-995 and S-095 catalysts in fixed-bed operation, the gas treated being a flue gas composition representative for gas-fired installations:

O_2	2 %v
H_2O	15 %v
CO_2	7 %v
N_2	76 %v

At 160 °C and a GHSV of 25 000 $Nm^3/(m^3.h)$ the NH_3/NO_x ratio was varied between 0.3 and 0.9. The kinetics of the deNOxing reaction with NH_3/NO_x <1 are complicate since each one of the components NO, NH_3, O_2 and H_2O is involved. The reaction order in NO is close to 1 while the order in NH_3 appears to be lower than 1. Water has a strong inhibiting effect. A typical result, demonstrating the high activity of the catalyst, is that, at a NH_3/NO_x ratio of 0.5, the conversion of ammonia was 58 %.

A semi-industrial test facility was constructed as a slip-stream unit in the flue gas system of a commercial gas-fired ethylene cracker plant. A test run was performed with some 300 l of S-995 catalyst (3 mm spheres) in fixed-bed reactor configuration. The run length was 6 months and excellent activity and stability were observed. Typical performance data are:

Temperature,	°C	135 - 155
GHSV,	$Nm^3/(m^3.h)$	2500 - 3500
NH_3/NO_x ratio		0.6 - 0.8
NO_x conversion,	%	60 - 80
NH_3 slip,	ppmv (dry basis)	< 5

The presence of sulphur dioxide in the flue gas is a major factor in determining the lowest possible operation temperature. According to the literature, at a given temperature and given water and ammonia concentrations it is the amount of sulphur trioxide which determines whether deposition of solid ammonium (hydro)-sulphate will occur. Apart from traces of SO_3 already present in the flue gas, the main proportion of sulphate seems to be formed from SO_2 over the deNOxing catalyst. Preliminary studies indicated the tolerable sulphur dioxide levels at various temperatures. They are given in Figure 2. The poisoning of the catalyst by ammonium (hydro)sulphate is reversible. The activity can be restored by operation at increased temperature.

REACTOR

For applications where dust is present in the flue gas and/or pressure drop must be minimised we have developed a patented Parallel Passage Reactor. Its principles are shown in Figure 3. It has been tested in both laboratory and semi-industrial installations with low-dust flue gas.

A study of the mass transfer steps involved is in hand. This provides background for the development of design principles for parallel passage reactors for different applications. Design variables are the reactor dimensions, relative catalyst and gas volumes in the reactor, the exchange surface area, catalyst particle size, etc. They can be adapted to the specific application depending on such factors as dust level, tolerable pressure drop, temperature, required deNOxing conversion, and ammonia slip.

APPLICATIONS

The first commercial Shell deNOxing unit will be installed in an ethylene cracker plant in West Germany, to come on stream in 1989. Here the low-temperature deNOxing technology will be applied.

We intend to extend the applications to other fields. The Shell low-temperature technology may be of particular interest where removal of dust and sulphur dioxide is performed upstream of the deNOxing unit. Overall optimisation of processes for the removal of sulphur, dust and NO_x appears to be an attractive possibility.

REFERENCE

1. M.J. Groeneveld, G. Boxhoorn, H.P.C.E. Kuipers, P.F.A. van Grinsven, H. Gierman and P.L. Zuideveld. Proceedings of the 9th International Congress on Catalysis, Calgary, Canada, 1988, Vol. 4, p. 1743 (paper 223-A).

GLOSSARY OF ABBREVIATIONS

GHSV, $Nm^3/(m^3.h)$	Gas hourly space velocity
SCR	Selective Catalytic Reduction
SEM	Scanning electron microscopy
TEM	Transmission electron microscopy
XPS	X-ray photoelectron spectroscopy
XRD	X-ray diffraction

Table 1

STANDARD ACTIVITY TEST FOR DENOXING CATALYSTS

Equipment:	Fixed-bed tubular reactor; catalyst volume 60 ml	
Test gas composition:	O_2	5 %v
	N_2	76 %v
	CO_2	13 %v
	H_2O	6 %v
	NO ~ 450 ppmv	
	NH_3/NO ratio = 1.5(v/v)	
Reaction conditions:	Temperature	150 °C
	GHSV	4000 $Nm^3/(m^3.h)$ (basis catalyst volume)

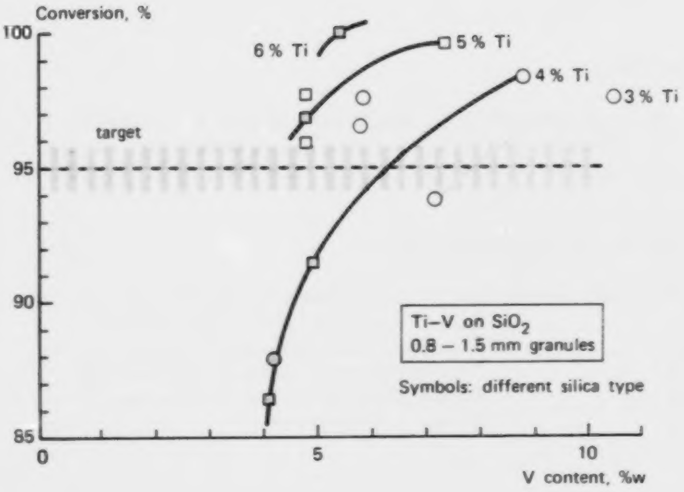


Figure 1. S-095 catalyst: effect of metal load on deNOxing activity (% conversion) in standard activity test

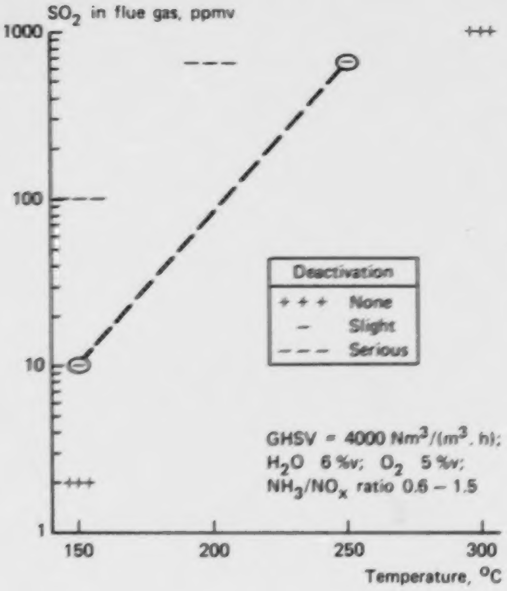
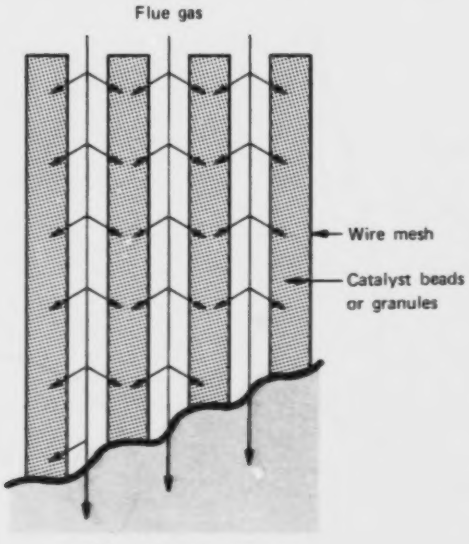


Figure 2. Deactivation of S-995 deNOxing catalyst by SO_2



Schematic view of a vertical cross–section

Principles

- Stationary catalyst
- Gas + dust flows through open channels
- Reactants transported radially to catalyst, (mainly) by diffusion

Figure 3. Parallel-Passage Reactor

NO_x Reduction of Waste Incineration Flue Gas

Bo Herrlander
Fläkt Industriella Processer AB
S-351 87 Växjö

ABSTRACT

Catalysts for NOx reduction have been tested at 610°F and 480°F in a tail end SCR-system after a waste incineration plant equipped with a CDAS-system for acid gas removal. The catalysts operated at 610°F showed no deactivation after 2300 hours but the catalyst operated at 480°F showed a slight deactivation. The ammonia injection control system was able to follow the very quick concentration variations after waste incineration. No formation of dioxines or laughgas over the catalysts was proven. The operation of the plant was trouble free and there was no fouling of the heat exchanger surfaces.

BACKGROUND

Waste incineration with effective flue gas cleaning is a route increasingly used to get rid of waste, mainly due to lack of space for landfill. Flue gas cleaning has up till now focused on acidic gases and heavy metals as well as dioxines removal. However, the NO_x emission from a waste incineration plant is considerable. The specific emission (lb/Btu) from waste incineration, is in the same range as for coal fired power plants. Further the operating time per year is often very high. NO_x emissions contribute to the acid deposition as well as photochemical smog.

INTRODUCTION

The waste incineration plant Munich South in Bavaria has to meet very stringent emissions. The two incinerators will take 40 tons/hour waste each, creating a flue gas flow of 141 260 scfm. The energy released is used to produce electricity as well as district heating. The plant is operated more than 6 500 h/year. The requirement for flue gas cleaning is HCL-removal 99.2%, SO_2-removal 95.2%, NO_x-removal 89% and particulate removal 99.95%. The corresponding emissions are HCL less than 0.004 gr/scf, SO_2 less than 0.011 gr/scf, NO_x less than 0.031 gr/scf and particulates less than 0.004 gr/scf. The flue gas cleaning is a retrofit and will be started January 1990. The acidic gases and particulates will be removed in a conditioned dry adsorption system (CDAS) and the NO_x will be removed in a SCR-system (DENIT). The CDAS-system is operated with hydrated lime and consists of a fluidized bed reactor and a fabric filter. The DENIT-system is connected after the CDAS-system to avoid catalyst poisons.The DENIT-system performance is highly integrated with the catalyst performance. In order to demonstrate an acceptable catalyst lifetime and system performance especially the ammonia injection control, the Kempten pilot plant was built.

Preceding page blank

SCR PILOT

In unit No.3 in Kempten the waste is fired in a conventional stoker furnace followed by a steam boiler where the flue gases are cooled down to about 390°F. The steam boiler is followed by the conditioned dry adsorption reactor where the flue gases are further cooled down to about 280°F and fabric filter. From this point a slip stream of 1500scfm is diverted to the pilot plant. The pilot plant cosists of a heat exchanger and 3 parallel reactor lines. Each reactor has a capacity of 7 ft^3 of catalyst. After the heat exchanger, an electrical heater brings the temperature up to final reaction temperature. Just after the electrical heater, before the reactor, ammonia is introduced in a nozzle arrangement. A static mixer ensures a good mixing and even distribution of ammonia and NO_x. In the reactors the gas is evenly distributed over the whole catalyst surface, by means of guidevanes. The reactor is equipped with electrical heat tracing elements and good thermal insulation to avoid heat losses and temperature gradients. The pilot plant was started February 2, 1988.

ANALYSER SYSTEM

Water vapour, nitrogen oxide, nitrogen dioxide, sulphur dioxid and oxygen are continuously monitored before and after the reactors.It is also possible to measure in between the catalyst layers. The sulphur trioxide and ammonia slip are analyzed manually from gas samples.

PILOT TEST PROGRAM

Objectives

- To demonstrate acceptable catalyst life, i.e. deactivation rate.
- Reactor temperature optimization.
- Optimization of ammonia injection control to follow the very fast NO_x concentration variations.
- Verify a trouble-free heat exchanger operation.
- Check for dioxine and N_2O formation over the catalyst.

Conditions - technical data

- Reactors in parallel		3
- Nominal gas flow per reactor	scfm	600
- Nominal reaction temperature	°F	480 - 610
- Inlet concentration at 10% O_2		
- NO_x	ppm	200-250
- HCL	ppm	about 30
- SO_2	ppm	about 30
- SO_3	ppm	< 1
- Particulates	gr/scf	< 0.002
- NO_x reduction degree	%	> 90

Catalyst activity is defined as $k = - AV \ln(1-x) = -(SV/Y) \ln(1-x)$ at SR = 1
AV = area velocity = fluegas flow/catalyst surface ($ft^3/ft^2 \cdot h$)
SV = space velocity (1/h) = $AV \cdot Y$
Y = catalyst surface/volume
x = reduction degree
SR = stoichiometric ratio (NH_3/NO_x)

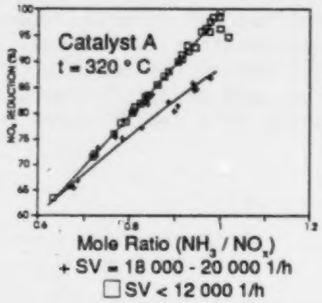
Catalysts

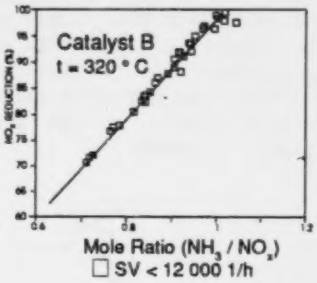
All tested catalysts are of parallel flow type, both honeycomb and plate catalysts have been tested in the pilot. The pitch varies between 1/8 - 1/6 inch. All tested catalysts are of high activity type.

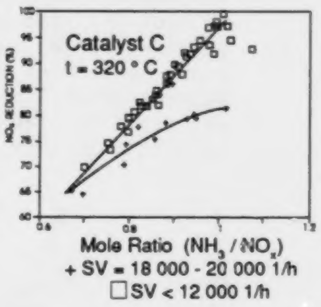
TEST RESULTS

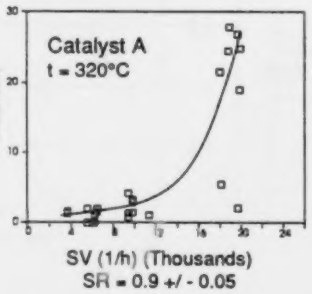
Catalyst response curves

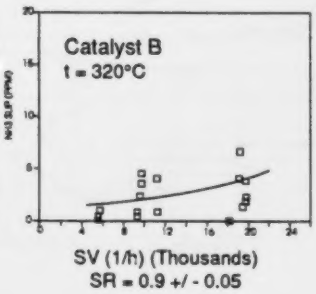
Response curves for the three catalysts in the first test period are shown below. Catalyst B shows an almost theoretical dependency between mole ratio and NO_x reduction at least up to a space velocity (SV) of 20 000 1/h. At low SV-values the NH_3-slip is very small but at a certain value the slip increases very rapidly indicating a decrease in NO_x reduction from the theoretical value.

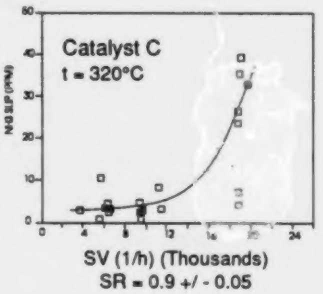












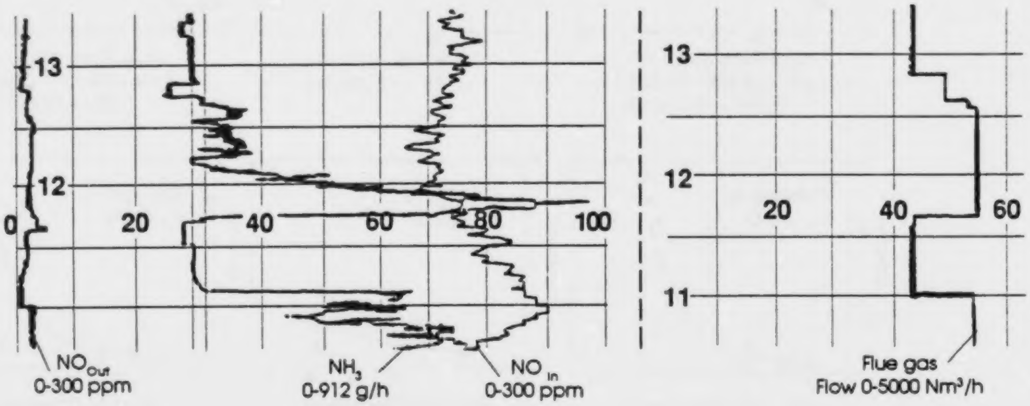
Catalyst deactivation

In the first test period the catalysts were operated with fixed SR-setting at 610°F for 2 300 hours. The catalysts were then removed and tested in a laboratory for determination of activity. The three catalysts did not show any deactivation. In this application there is a fear for deactivation due to pore condensation of salts, like ammonium sulphates and zink chloride. Also alkali metals, mercury, arsenic, led etc. (1), may cause deactivation. It has been shown at several plants, that the dry adsorption system has a far better heavy metal removal than the wet scrubbing system (2). Fast catalyst deactivation mainly from lead has been observed in test plants after wet scrubber systems.

In the second test period the temperature was lowered to 480°F. The catalysts in this test run showed a minor deactivation loss. After 2 200 hours the catalysts show between 98-99% of their virgin activity. It was however not possible to fully modify the catalyst activity in order to compensate for the lower operating temperature. The system economics for the lower operating temperature alternative is therefore questionable.

Ammonia injection control system

It was possible to show that the ammonia injection control system was able to follow the very quick concentration variations as well as load changes. This is shown in the figure below. A load change up and down is simulated by a momentare flow change. The concentration variation maybe as quick as 0.5 ppm/s without any load changes. This change may continue for several hundred seconds. If the load change is taken into consideration, the actual change might be as high as 1 ppm/s. The catalyst will adsorb the ammonia. This adsorption will be highest on a virgin catalyst and gradually decrease with deactivation. The chosen control system consists of a feed-forward trim back ammonia injection control system.



Dioxin formation

Dioxins were measured before and after the catalyst. On both sides the concentrations were very low (calculated in dioxin equivalents according to Eadon $< 4.4 \cdot 10^{-6}$ gr/scf). The conclusion is that there is no production of dioxins over the catalyst (3). It is a well known fact that dioxins may be reformed between 1060°F and 1710°F (4, 5), may be catalyzed by fly ash. In this case, however, both fly ash and HCL is removed to a very large extent.

Laugh gas

Gas samples were taken both from upstream and downstream of the catalysts and analyzed for laughgas, N_2O. No laughgas was found in these samples. Used methods detection limit is 5 ppm. Also by others no laugh-gas has been detected (6).

Heat exchanger operation

The heat exchanger operation was trouble-free. Every inspection showed clean surfaces and no dust build-up. A slight corrosion was observed due to dew point passage with the following condensation at every start-up. The heat exchanger is of a non-leakage type with the gas to the reactor going on the tube side and gas from the reactor on the shell side.

REFERENCES

1. Energi Spektrum vol. 6, June 1987, p. 50 - 59 "Indizien process"

2. Energi ur avfall, Statens Energiverk, 1986:6, ISBN 91-38-09453-3

3. Energi Miljö Konsult Malmö: "Measurements of dioxine and other chlorinated aromatics at Fläkt SCR DeNox-plant, Kempten, Bavaria" Malmö 1988-09-28

4. JAPCA, No. 12, vol. 37, December 1987, p. 1451 - 1462 A comparison of Dioxine, Furan and combustion Gas data from Test programs at three MSW incinerators

5. MKS Studsvik: "Measurements of dioxine and other chlorinated aromatics" 1987-11-24

6. BWK Bd. 37 (1985) No. 12, December, p. 465, "Kein N_2O durch japanische Entstichungskatalysatoren"

REBURNING AND REPOWERING FOR NO_x CONTROL ON LARGE UTILITY BOILERS

S. L. Chen, E. C. Moller, D. W. Pershing
Energy and Environmental Research Corporation
Irvine, California

and

A. B. Walters
Florida Power & Light Company
Juno Beach, Florida

ABSTRACT

Tests conducted in a 3 MW_t pilot scale facility indicate that NO_x emissions can be reduced by at least 50 percent through the application of natural gas reburning, even in oil-fired boilers, such as the Florida Power & Light's 800 MW_e units, with relatively tight residence time limitations. Particulate emissions were found to be strongly dependent on burnout zone stoichiometry; however, above 2 percent excess O_2 the emission levels were identical to those achieved without reburning. SO_3 emissions were found to increase with the application of reburning, but this effect can be partially mitigated by distributing the addition of the burnout air. Repowering existing steam generation units with combustion turbines decreases thermal NO_x formation due to reduced local flame temperatures and provides a mechanism for incinerating a portion of the NO_x generated in the combustion turbine. Repowering alone produces 35 percent reductions in NO_x emissions and repowering in conjunction with reburning results in over 70 percent NO_x reductions.

REBURNING

Combustion of fuel oil produces NO_x, SO_x and particulate emissions. Combustion conditions, such as excess air, which tend to promote high carbon burnout and good flame stability also promote the formation of NO_x and SO_3. Conversely, the control of NO_x emissions through control of the combustion process may have an adverse impact on carbon burnout. Reburning involves the injection of secondary fuel and air downstream from the main combustion zone. Reburning is an attractive concept because it allows the primary combustion zone to be operated, independently from the secondary reburning zone, at conditions which optimize flame stability and carbon burnout.

An experimental study(1) was undertaken to optimize the use of natural gas reburning for the control of NO_x as well as unburned carbon and SO_3 emissions from

Preceding page blank

oil fired boilers. Parametric experiments were conducted in a 3.0 MW_t pilot scale facility configured to simulate the thermal and emissions characteristics of an 800 MW_e boiler at FPL, particularly the short residence time (approximately 500ms) available between the upper burner and superheater tubes.

OPTIMUM AIR DISTRIBUTION

Figure 1 summarizes the influence of the excess oxygen concentration in the burnout zone. NO_x, particulate, and CO emissions are shown as a function of excess O_2 in the exhaust for both baseline (uncontrolled) oil combustion and for an equivalent level of oil firing with an additional 20% natural gas reburning. NO_x reductions in excess of 50% were achieved at all excess oxygen levels; above 2% exhaust O_2, the application of natural gas reburning had no detrimental effects on either particulate or CO emissions. Below 2% O_2, the application of natural gas reburning resulted in increased particulate and CO emissions, almost certainly due to the presence of the fuel rich reburning zone which produced unburned carbonatious fragments that were not completely burned out at these low NO_x excess oxygen levels. The Figure 1 data indicate that the final exhaust oxygen should remain at approximately 2% excess O_2 to minimize thermal losses and NO_x emissions while still achieving good carbon burnout. Thus, the recommended stoichiometry distribution for the application of reburning in limited residence time, oil fired systems would be: $SR_1 = 1.1$, $SR_2 = 0.9$, and $SR_3 - 1.1$.

This study revealed a previously unknown complication; the application of reburning with oil firing can produce a significant increase in SO_3 emissions if the system is not fully optimized(1). Enhanced SO_3 formation appears to result from homogeneous oxidation of SO_2 by O atoms which are produced during the low temperature oxidation of CO in the final burnout zone. This effect can be significantly mitigated by distributing the addition of the burnout air to provide at least two approximate steps in the stoichiometry change from $SR_2 = 0.9$ to $SR_3 = 1.1$. Splitting the burnout air into two streams has essentially no effect on any of the other emissions.

REPOWERING

Repowering existing steam turbine generation units with combustion turbines (CT's) to create combined-cycle operation can produce heat rate reductions of up to 18 percent and provide additional unit capacity with low capital expenditure relative to the cost of completely new power plant additions(2). Combustion turbine repowering with a supplemental boiler is attractive from an NO_x emissions standpoint because it decreases thermal NO_x formation due to reduced local flame temperatures, and provides a mechanism for incinerating a portion of the NO_x generator in the combustion turbine.

Tests were conducted in a 3.0 MW_t pilot scale facility to evaluate natural gas reburning for NO_x control in a partially CT repowered 800 MW_e boiler at FPL. The combustion turbine exhaust was simulated using a natural gas fired preheater. The initial studies focused on characterizing the differences between normal and repowered operation. Subsequent experiments were conducted to evaluate the applicability of standard reburning for NO_x control in the repowered configuration and to assess the potential of advanced reburning concepts using selective NO_x reduction.

Influence of Repowering

The effect of repowering on NO_x emissions is significant. As illustrated in Figure 2, repowering alone produced a 35-percent reduction in NO_x emissions on a lbs NO_x/MBtu basis with a No. 6 oil primary and reductions in excess of 70-percent with a natural gas fired primary. With both fuels, a major portion of the reduction is associated with primary boiler incineration of the NO_x generated in the CT. Both theoretical calculations and experimental measurements suggest that the temperature profile in the boiler should be approximately 200°F cooler with a repowered configuration, and this caused a significant reduction in NO_x levels with a natural gas primary, but had little influence when heavy oil was the primary fuel. Data obtained also suggest that the dramatic NO_x reduction with repowering is achieved without detrimental effects on SO_3 emissions or carbon burnout at excess oxygen levels above 2-percent. Increasing the NO_x levels in the CT exhaust increased the overall NO_x emissions; however, this effect was somewhat mitigated by incineration of approximately 40 percent of the CT NO_x as it passed through the primary flame of the boiler.

Application of Reburning

Reburning was also found to be effective for NO_x control in the repowered configuration; reductions of approximately 50 percent were achieved under typical FPL CT-repowering conditions(3). In addition, carbon burnout was not influenced by repowering with reburning, but SO_3 emissions were lower in the repowered configuration compared to the reburning case with air as the oxidant (due to the lower oxygen partial pressure and lower temperature of the burnout zone). Use of an advanced reburning configuration(4) in conjunction with $(NH_4)_2SO_4$ injection produced NO_x emissions below 100 ppm in the repowering configuration while good carbon burnout and low SO_3 levels were also maintained as illustrated in Figure 3. Overall, an 80-percent reduction from the uncontrolled emission levels was obtained by using 10- or 20-percent reburning in conjunction with selective NO_x reduction with $(NH_4)_2 SO_4$ and repowering.

REFERENCES

1. Moller, E. C., S. L. Chen, D. W. Pershing and A. B. Walters. "Optimization of Natural Gas Reburning for Controlling Pollutant Emissions From Oil Fired Boilers", presented at Spring Meeting, Western States Section/The Combustion Institute, March, 1988.

2. Walters, A. B., J. R. Craig, R. J. Cullen, R. E. Herbster, and J. A. Van Laar. "Gas Turbine Repowering Considerations", Feasibility Study for Florida Power and Light Company, 1987.

3. Moller, E. C., S. L. Chen, D. W. Pershing and A. B. Walters. "Reburning For NO_x Control in Combustion Turbine Repowering", presented at Fall Meeting, Western States Section/The Combustion Institute, October, 1988.

4. Heap, M. P., S. L. Chen, J. C. Kramlich, J. M. McCarthy and D. W. Pershing. "An Advanced Selective Reduction Process for NO_x Control", Nature, Vol. 335, Issue 6191, 1988.

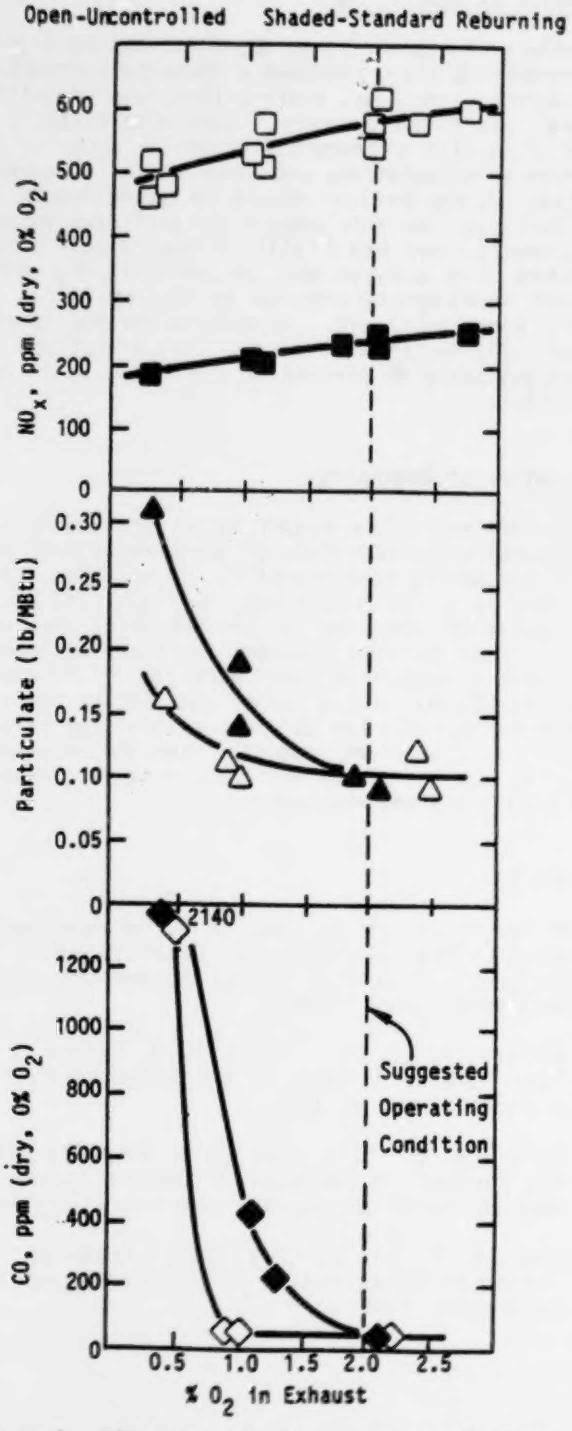


Figure 1. Effect of exhaust oxygen on emissions.

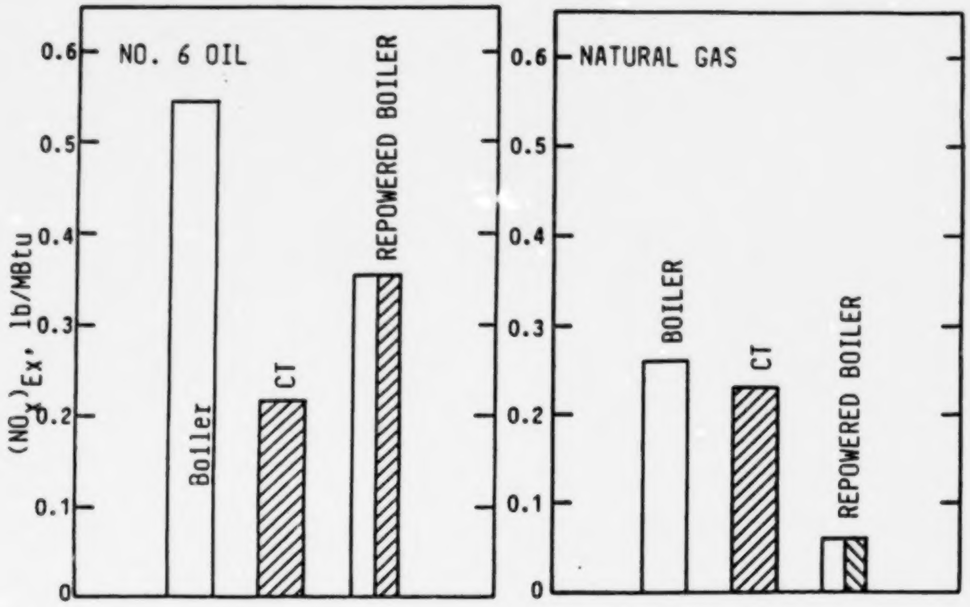


Figure 2. NO_x mass emissions.

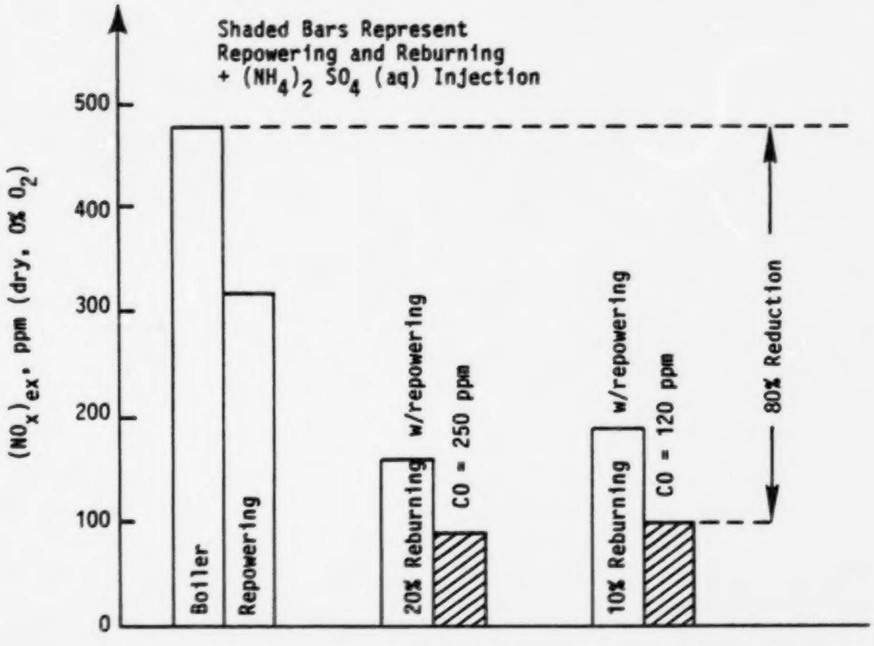


Figure 3. Effectiveness of advanced reburning.

Session 9

OIL AND GAS COMBUSTION APPLICATIONS

Chairman: A. Kokkinos, EPRI

RETROFIT OF AN ADVANCED LOW-NOx COMBUSTION SYSTEM AT HAWAIIAN ELECTRIC'S OIL-FIRED KAHE GENERATING STATION

J. L. B. Yee
R. B. Freitas
Hawaiian Electric Company, Inc.
Honolulu, Hawaii

D. V. Giovanni
S. E. Kerho
Electric Power Technologies, Inc.
Berkeley, California

M. W. McElroy*
Electric Power Research Institute
Palo, Alto, California

ABSTRACT

Hawaiian Electric Company, Inc. (HECO) completed major combustion system modifications in mid-1988 on Kahe Unit 6, a Babcock & Wilcox (B&W) oil-fired unit rated at 146 MW. The modifications were undertaken to reduce emissions of oxides of nitrogen (NOx) and particulate matter (PM), and to restore operational flexibility that had been impaired with burners-out-of-service operation previously used for NOx control. Modifications included B&W primary gas dual register burners (PG-DRB), front-wall and rear-wall overfire air ports, extensive ductwork for the overfire air and recirculated gas flows, revision of the oil atomizing steam system, and enhancements to the automatic burner control system. The installation of the PG-DRB low-NOx burners represents the first application of this type of combustion system to a utility boiler in the United States.

In conjunction with the modifications, a comprehensive testing program under the joint sponsorship of the Electric Power Research Institute and HECO was conducted to characterize emissions and operations before and after the modifications. The test program, test results, retrofit costs, and a preliminary extrapolation of results to industry-wide application are summarized. HECO's operating experience with the combustion system modifications in attempting to reduce NOx and PM are also discussed.

* Now with Electric Power Technologies, Inc., Menlo Park, California

INTRODUCTION

In January 1979, the Hawaiian Electric Company was granted a Prevention of Significant Deterioration (PSD) permit by the U.S. EPA for the construction of an oil-fired steam-electric generating unit (Unit No. 6) at the Kahe Generating Station. The permit specified NOx emission limits of 0.23 lb/MBtu (180 ppm at 3% O2) and particulate matter (PM) emission limits of 0.03 lb/MBtu. Since the commissioning of Kahe 6 in 1981, HECO has undertaken numerous emission reduction test programs to achieve compliance with these limits. These efforts, involving operational modifications and flue gas recirculation to the windbox, resulted in optimized NOx and PM emission levels for continuous operation of the boiler with the installed combustion equipment. Optimization included operation in a burners-out-of-service (BOOS) mode with 6 of 9 burners in operation, and with flue gas recirculation to the windbox, resulting in typical NOx emissions of 0.28 lb/MBtu and PM emissions of typically 0.06 to 0.08 lb/MBtu (with excursions above 0.9 lb/MBtu).

In July 1987, HECO contracted with The Babcock & Wilcox Company to design, install, and commission state-of-the-art retrofit low-NOx combustion technology at Kahe 6. The emission guarantees were 0.23 lb/MBtu NOx as NO2 (specified for a fuel nitrogen content of 0.5%) and 0.1 lb/MBtu for PM emissions. Additionally, it was intended that the retrofit technology would allow a return to all-burners-in-service (ABIS) operation, thereby improving the operating flexibility and generating capabilities of the unit which had been impaired with BOOS operation. Specifically, a higher turndown was expected from improved flame stability at low loads (the lowest load for dispatch was 95 MW with BOOS), and a higher reliability in achieving full load was expected with the ability to accommodate burner maintenance outages without load reduction (with BOOS, shutdown of an additional burner would reduce generating capacity). This retrofit, the subject of this paper, is the first installation in the United States of the integrated application of low-NOx burners, flue gas recirculation (FGR) and overfire air (OFA) to a heavy oil-fired utility boiler. The specific combustion system, designated "PG-DRB", is licensed by B&W from Babcock-Hitachi (BHK) who commercialized the technology in Japan.

HECO retained Electric Power Technologies, Inc. (EPT) to work in cooperation with HECO Engineering, Environmental, and Production Departments for implementation of the retrofit project. In this capacity, EPT participated in the specification, design review, and startup of the equipment, and acted as technical liaison between HECO and B&W. In addition, HECO and the Electric Power Research Institute (EPRI) jointly sponsored an independent test program to document the performance of the retrofit low-NOx technology. EPT was retained by HECO to coordinate the test program and was responsible for implementing the tests at Kahe, reducing the data, and interpreting the results. The performance of the original combustion system for both ABIS and BOOS operating modes were characterized in a "baseline" test series that was conducted in early 1988, immediately prior to the outage for installing the new equipment. Following B&W's commissioning of the new equipment in September 1988, a comparative "post-retrofit" test series was conducted.

This paper presents the results of the test program, including a discussion of the baseline and post-retrofit emission results, a synopsis of the start-up and operational experiences with the new combustion system, and a preliminary assessment of the costs and applicability of the technology. A formal documentation of this program will be provided in an EPRI final report to be prepared later in the year.

DESIGN AND OPERATION OF ORIGINAL EQUIPMENT

Kahe 6 is an oil-fired steam-electric unit rated at 146 MW (gross). The boiler is a radiant reheat type, manufactured by B&W (refer to Figure 1 for an elevation view). For NOx control, the boiler was originally equipped with nine B&W dual register burners arranged in a 3 x 3 array on one wall, and flue gas recirculation (FGR) to the windbox which permitted up to 20% of the flue gas to be mixed with combustion air prior to the burners. The dual register burners were intended to provide delayed mixing of the oil and air which would result in lower NOx. The design was based on B&W's dual register burners developed for coal-firing. The FGR acts as a thermal diluent, suppressing peak flame temperatures and reducing NOx formation. From 1971, when Kahe 6 was originally designed, to 1978 when the design was processed by EPA for Best Available Control Technology, this combustion system represented state-of-the-art technology available from U.S. boiler manufacturers.

When the unit was commissioned to service with all nine burners in-service, the NOx emissions were found to exceed the operating permit limit (i.e., the PSD permit limit of 0.23 lb/MBtu) by a considerable margin. In order to minimize NOx, Kahe was operated with flue gas recirculation and only six active burners in a BOOS mode. BOOS operation effectively stages the combustion -- the six active burners operated fuel rich and the air entering through the idle burners was mixed with the combustion products later in the furnace to complete the combustion process.

DESCRIPTION OF COMBUSTION SYSTEM MODIFICATIONS

The new low-NOx combustion system consists of seven main elements:

- PG-DRB burners,
- Improved oil atomizers, and the use of constant differential pressure steam atomization,
- Utilization of existing flue gas recirculation (FGR) to the windbox combustion air,
- "Primary gas" (PG) -- flue gas recirculation directly to the burners (unmixed with the combustion air),
- Overfire air (OFA) system,
- Upgrading of the Bailey 860 burner controls, and
- Modification of the FGR and combustion controls.

The PG-DRB burner, shown schematically in Figure 2, is an improvement upon the 1st generation B&W dual register burner originally installed at Kahe 6. It includes improved aerodynamics (changes in throat diameter, air distribution and swirl, a new air register design, etc.) for enhanced NOx reduction, and the introduction of pure recirculated flue gas through an annular sleeve between the core air and secondary air exits of the burner. In principle, PG serves to "blanket" the base of the oil flame to reduce the availability of oxygen during the initial phases of combustion (Ref. 1). The burners were supplied with new wall panel sections, flame scanners/ignitors, and complete burner front control and piping assemblies. The burners also included unique on-line air flow rate monitoring capability which eliminated the need for windbox compartmentalization. The firing system was intended to burn a variety of fuel oils with sulfur content limited to 0.5%, and fuel nitrogen content varying up to 0.5%

To help ensure minimum particulate emissions, HECO requested B&W to supply an oil atomizer that would operate at constant atomizing steam-to-oil differential, and provide a higher quality (smaller drop diameter) spray than that produced by the existing Racer design (The Racers operated with a constant steam pressure as the oil supply pressure varied with load). In response, a Y-jet steam atomization system was originally supplied with the PG-DRB burner, which provided atomizing steam at a higher flow rate than Racers.

The unit's existing FGR system was adequate for supply of FGR to the secondary air and was left intact, except for modified controls. However, to provide flue gas to the burner PG annuluses, additional piping (including a distribution system within the windbox) was required to convey flue gas to each burner from the main FGR duct. The piping was equipped with orifice meters and butterfly valves to permit on-line monitoring and control for PG to each burner.

The overfire air system was designed to divert up to 30% of the total combustion air to six OFA ports located on the front and rear boiler walls (three ports per wall), approximately 10 feet above the top burner elevation. Each OFA port was equipped with damper assemblies and air spin vanes to enable independent control of air quantity, velocity and furnace penetration. A schematic showing the port design is provided in Figure 3. Installation of the ports required elaborate ductwork, windbox, and boiler water wall modifications. Like the burners, the OFA ports were equipped with flow rate monitors, enabling accurate on-line measurement of separate flows through the spin annulus and central core of each overfire air port.

Flow modeling of the windbox and furnace was an integral part of the engineering design effort by B&W. A 1/8th scale model of the windbox was built and tested to ensure that equal flow to the burners would be achieved with the internal windbox changes caused by the new burners and PG distribution system. A separate 1/8th scale model of the furnace was then constructed and tested to establish placements and design for the OFA ports for optimum mixing. The decision to use six ports (instead of three) and a 70:30 rear-to-front wall distribution of overfire air was based on the modeling results. In addition, individual burners and overfire air ports were flow calibrated at full scale prior to shipment to facilitate air flow adjustment and balancing during startup, commissioning, and emission testing.

DESCRIPTION OF EMISSION TEST PROGRAM

The HECO/EPRI emission test program consisted of a pre-retrofit baseline test series, and a post-retrofit test series that followed B&W's start-up of the new combustion equipment. The testing was also complemented by a documentation of the retrofit costs, and an evaluation of the test results and costs as they may pertain to the other utility oil-fired boilers. Specific objectives of the testing were:

Baseline tests -- Establish a basis for comparing boiler and emission performance before and after the combustion equipment modifications. Data were developed to enable quantitative comparisons over the load range in terms of: NOx, PM total mass, stack opacity, CO, and SO3 emissions; excess air level and O2 balance; boiler efficiency; maximum load capability; turndown; achievement of design steam conditions; fuel properties; and other operational factors. The baseline tests included parametric testing during ABIS and BOOS operation with variations in boiler load, excess O2 level, FGR rates, and fuel nitrogen concentration. Particulate matter size distribution and composition analyses were also performed at full load conditions.

Post-retrofit tests -- The objectives were multi-fold: (1) Characterize boiler and emission performance for the operating conditions prescribed by B&W and compare them with the baseline conditions, (2) Systematically evaluate the independent and combined effects of low-NOx burners, OFA, FGR, and PG on NOx emissions, (3) Quantify changes in PM emissions for operating conditions corresponding to different NOx emissions, and (4) Identify potential improvements in operation compared to operating modes resulting from startup and commissioning.

Emissions testing utilized state-of-the-art extractive sampling equipment and methodology, including multi-point gas traversing at the economizer outlet. Testing was performed through the cooperative efforts of personnel from the HECO Environmental and Production Departments, B&W, Tenerex, and Mullins Environmental Testing Company, with overall testing being coordinated and directed by EPT.

STARTUP AND COMMISSIONING OF MODIFIED COMBUSTION SYSTEM

The new combustion system posed a large number of variables that could effect the NOx and PM emissions of the unit:

1. Burner:
   a. Outer spin vane position
   b. Inner spin vane position
   c. Core air flow
   d. Secondary air flow
   e. Oil flow rate
   f. Axial position of the oil gun impeller relative to the atomizer
   g. Axial position of the impeller relative to the burner throat

2. Atomizer:
   a. Atomization approach (i.e., basic tip design)
   b. Steam/oil pressure differential
   c. Oil supply pressure
   d. Oil viscosity (measured via on-line viscosity meter)
   e. Spray cone angle
   f. Number of exit holes and their arrangement
   g. Steam-to-oil mass ratio

3. FGR:
   a. Amount of FGR mixed with the combustion air

4. PG:
   a. Amount of PG supplied to the individual burners

5. OFA:
   a. Percent of total air supplied to the OFA ports
   b. Percent of total OFA supplied to front OFA ports
   c. Percent of total OFA supplied to rear OFA ports
   d. Air flow balance among front OFA ports
   e. Air flow balance among rear OFA ports
   f. Air flow split between core and annulus of each OFA port
   g. Spin vane setting of each OFA port

As is apparent from the number of variables listed above, the PG-DRB system is complicated and proper adjustment requires a comprehensive startup program. Moreover, for wall-fired boilers, the emissions are significantly impacted by the respective performance of individual burners. Therefore, proper tuning of the boiler dictated that the combustion be optimized for each burner and the system as a whole.

B&W performed the commissioning of the retrofit equipment in cooperation with the HECO Production Department. The commissioning required 12 weeks (2 shifts/day, 7 days/week), and consisted of the following elements: startup; evaluation of atomizers; parametric testing and optimization; and acceptance testing.

During startup, it was immediately apparent that there was a significant trade-off between NOx and opacity whenever staging or low excess air operation was attempted. Achieving NOx below the level of 0.23 lb/MBtu simultaneously with opacity below 20% proved to be infeasible. Despite the use of Y-Jet atomizers, the major contribution to the problem was determined from field testing and laboratory spray characterization tests to be atomization quality (i.e., the oil drops were too large and the spray pattern was not uniform). This necessitated an evaluation of several different B&W atomizer designs in the PG-DRB burner.

Several different B&W atomizers were tested including modified Racers with increased steam rates, Y-Jets and T-Jets with different spray cone angles, Babcock-Hitachi "D-tips", and a developmental I-Jet design. These atomizer types are characterized by their geometry, atomizing steam-to-oil mass flow rates, the the size of oil drops produced. For oil properties and operating conditions at Kahe, the nominal Sauter Mean Diameter (SMD) of oil droplet size distributions were 400, 300 and 225 microns for the Racer, Y-Jet and T-Jet, respectively. The T-Jet was judged to be the best atomizer design available to B&W for use with the PG-DRB burner, and parametric and optimization tests performed with this tip demonstrated that emission guarantees (0.23 lb/MBtu NOx and 0.1 lb/MBtu PM) could be met. The atomizing steam consumption with the T-Jet is 15 to 20 times that normally used with the original Racer tips.

The acceptance tests were performed under the following operating conditions recommended by B&W: 10% FGR to the windbox, minimum (<2%) PG flow to the burners, 27% of the total air to the overfire air system (split 70% to the rear ports and 30% to the front ports), and an average excess O2 at the economizer of 3%. Under these conditions while firing a 0.35% nitrogen fuel oil, NOx emissions at a maximum load of 156 MW (steam valves wide open, slight overpressurization) and at 62 MW (the guarantee 2.5:1 turndown point) were 0.207 and 0.175 lb/MBtu, respectively. Corresponding particulate emissions were 0.074 and 0.085 lb/MBtu, respectively. These results typified the best overall emission performance achieved in the 12-week startup period.

PRE-RETROFIT (BASELINE) EMISSIONS

The discussion below provides a very brief overview of the baseline results. More detailed presentations of key baseline test data are provided in the following section where they are compared directly with post-retrofit data.

NOx Emissions

Typical NOx emissions for the original equipment at Kahe 6, when operated at high load and with a nominal fuel nitrogen level of 0.3%, are illustrated in Figure 4. For ABIS operation without FGR, the NOx was typically 0.8 lb/MBtu (600 ppm). This NOx level is consistent with that observed for boilers of similar size and vintage, firing heavy oil, and equipped with single register burners. Hence, the burners at Kahe 6 did not produce low NOx that was expected for the dual register design. The addition of FGR reduced the NOx by nominally 50%. The significant magnitude of this reduction with FGR suggests that the burners were producing considerable "thermal" NOx when operated without FGR. This is a further indication that the dual register design was not effectively delaying the mixing of oil and combustion air.

Operation in the BOOS mode resulted in substantial NOx reductions when applied with or without FGR. With BOOS and 10% FGR the nominal NOx emission level was 0.28 lb/MBtu (approximately 220 ppm), or about a 65% reduction from the ABIS operating condition without FGR. Increasing FGR above 10% did not provide significant additional reductions in NOx, reflecting a relatively "steep" dependence of NOx on initial FGR rate.

Effects of Fuel Nitrogen on NOx Emissions

Fuel oils with nitrogen content ranging from 0.24% to 0.45% were tested to establish the influence of this parameter on NOx emissions. This range is typical of the fuel nitrogen variations normally experienced at the Kahe Station. Results at high load with FGR are compared in Figure 5 for both BOOS and ABIS operation. As can be seen, the fuel nitrogen has a substantial effect on NOx emissions. Under ABIS conditions, NOx emissions increased approximately 55 ppm for every 0.1% increase in fuel nitrogen. With BOOS, the sensitivity was reduced to about 35 ppm/0.1% nitrogen. These results are consistent with data in the literature which generally show a nearly linear NOx sensitivity to fuel nitrogen, and lower conversion rates of fuel nitrogen to NOx under slower mixed or staged combustion. The relatively high conversion rate, especially during ABIS operation, further substantiates the belief that the dual register burner design was not effectively producing delayed combustion.

The post-retrofit tests were performed with a relatively constant fuel nitrogen content averaging 0.35%. Thus there was not an opportunity to develop data on fuel nitrogen dependence for the PG-DRB system for comparison. Nevertheless, the baseline results are believed to constitute a unique set of data on the dependency of NOx on fuel nitrogen for a single unit operated with and without staged combustion. An analysis of the fuel oils used during the baseline and post-retrofit testing is provided for reference in Table 1.

Particulate Emissions

Particulate matter emissions were measured for both ABIS and BOOS operating modes for each of two oils. The PM total mass emissions ranged from 0.067 to 0.092 lb/MBtu which is consistent with levels measured by HECO during the 1981 to 1986 time period for Kahe 6. There was no significant difference in PM emissions between ABIS and BOOS; the above variation in emission levels is considered to be within the normal range of variation for this type of source and accuracy of the PM measurement method. Stack opacity was typically 4-6% during ABIS and BOOS operation.

Unburned carbon was the principal component of the PM. The carbon concentration ranged from 70% to 77% of the PM total mass. This level of unburned carbon was felt to be typical for a combustion system utilizing Racer atomizers and an SMD of 400 microns. The sulfate component was approximately 2% which is typical for low-sulfur fuel oil.

POST-RETROFIT EMISSIONS

Similar to the baseline test series, the post-retrofit testing involved an extensive, systematic variation of boiler and combustion system operating parameters. The discussion below focuses on the most significant findings: the effectiveness of FGR and PG in reducing NOx, the effect of OFA, NOx dependence on load, the trade-off between NOx and PM emissions, and the effect of the modifications on excess O2.

Effectiveness of Flue Gas Recirculation to the Windbox

The effect of FGR rate on NOx is compared in Figure 6 for baseline and post-retrofit operation. The FGR rate is defined as the amount of recirculated flue gas divided by the sum of the total air and fuel flows. The total reduction in NOx attributable to FGR with the new combustion system varies from 20% when OFA is used, to about 30% when the OFA ports are closed. FGR rates higher than approximately 7% are ineffective. The limited effectiveness of FGR as compared to pre-retrofit conditions is apparently due to the already lower NOx formation which occurs as a result of using OFA and the PG-DRB burners

Effectiveness of Flue Gas Recirculation to the Burners (PG)

The effect of PG flow on NOx is shown in Figure 7. The PG rate shown is percent flow, with 100% representing a PG flow equivalent to 5% FGR. PG has no effect on NOx below the 50% demand point. Increasing PG to approximately 80% results in a 9% decrease in NOx, with a corresponding increase in opacity from 13 to 16%.

Effect of Overfire Air

The effect of OFA level on NOx and opacity is shown in Figure 8. As can be seen, OFA is a very effective means of reducing NOx emissions. Use of 30% of the total air as OFA (the maximum possible for the system) results in a decrease in NOx of over 50%. The burner air/fuel ratio at maximum OFA is approximately 81% of stoichiometric.

The results in Figure 8 also illustrate the strong trade-off between NOx and opacity (more on this topic later). OFA levels of over 21% were required for this fuel to reduce NOx to 0.23 lb/MBtu (180 ppm), with resulting opacity levels of between 10-15%. Opacity levels in this range tended to be unstable. For example, at 30% OFA, the average value of opacity plotted was 17%, with peak-to-peak oscillations of 12-22%.

These results correspond to the OFA flow bias recommended by B&W (70% of OFA to rear wall, 30% to the front wall). Further biasing of the OFA to a 90%/10% split improved opacity and enabled operation at slightly lower furnace excess O2. It was further demonstrated that with balanced burner-to-burner flows (as verified by individual burner fuel and air flow measurements) and uniform air flows to the OFA ports, a balanced distribution of excess O2 across the furnace could be achieved. Thus, when the OFA and burner flows are accurately determined (as was the case here), furnace O2 distribution can be controlled quite well. Rarely does conventional burner front instrumentation provide the necessary measurements to accomplish this.Carbon monoxide emissions were typically less than 50 ppm during all post-retrofit test conditions, and did not correlate with opacity. Thus, they were not a prime consideration in establishing operating excess O2 levels.

NOx vs Load

The NOx emissions over the normal load range of the unit are shown in Figure 9, comparing baseline and post-retrofit results. Under baseline conditions, NOx increases with load up to the maximum load point. A similar trend is apparent for the new combustion system, but it is much less pronounced, except for an apparent rapid rise in NOx above 146 MW. The excess O2 at the economizer outlet for all the data in Figure 9 varies with load from about 3% at high load to about 6% at the lowest load.

NOx and Particulate Trade-off

The level of importance that the trade-off between NOx and opacity posed with regard to system optimization (refer to Figure 8) was unexpected from previous experience reported by Babcock-Hitachi (BHK) in Japan (over 5000 MW of PG-DRB is operational there). It appears that this trade-off is a fundamental feature of the PG-DRB system, when fired with heavy oils. Further assessment of the Japanese experience in the light of the HECO results led to a conclusion that a similar trade-off exists in Japanese installations, however, it is not an issue there because the boilers are equipped with electrostatic precipitators for particulate emission control. It is now suspected that the low NOx results reported from Japan by BHK were obtained by operating the burners and OFA system for low NOx, with resulting high opacity levels controlled by the precipitators which are installed on virtually all utility oil-fired boilers equipped with low-NOx combustion systems. The PG-DRB system configured with Racer atomizers per the Japanese experience could not meet the NSPS particulate standard (0.1 lb/MBtu) or opacity standard of 20% when operated in a low-NOx mode with >25% OFA and >10% FGR.

Particulate mass emissions measured during B&W acceptance tests were comparable to levels reported above for baseline conditions. However, it is very apparent from opacity readings during other tests that higher PM emissions can occur when the system is not operated under tuned conditions. Opacity levels are currently 10-15% as compared to 4-6% with the original combustion equipment.

Effect of Modifications on Excess Oxygen Requirements

Following the retrofit, slightly higher furnace excess oxygen levels compared to previous BOOS operation (by about 2-3 tenths of a percent) were required as primarily dictated by opacity considerations. The unit is currently operated with 3-3.5% excess oxygen at full load. The actual value varies from day to day as fuel properties vary and the operators adjust furnace combustion conditions to meet NOx and opacity limits. The increase in excess air, although small, was disappointing in that the retrofit was expected to result in reduced excess O2 operating requirements based on the Japanese experience and general improvements in combustion balance and control systems.

A summary of the post-retrofit NOx results is provided in Figure 10, including baseline data under similar fuel, load, and excess O2 conditions. Significantly, a 75% reduction was achieved with all burners in service with the PG-DRB system as compared to "uncontrolled" emissions with the original burners.

OPERATIONAL IMPACTS

The installation of the PG-DRB system led to a number of operational improvements. Some of these can be attributed to the general upgrading of the firing control system and the return to ABIS operation:

- The boiler turndown range increased due to a reduction in the minimum load from 95 MW to 50 MW that resulted from improved flame stability; the achievable rate of load change remained the same
- Ignitor reliability and flame scanning improved over the load range
- Full load operation can be maintained with up to two burners out of service for maintenance; Under previous BOOS operation, removing a single burner from service for maintenance would require a reduction in maximum load.
- Furnace excess O2 balance across the economizer outlet improved to within <1.0% O2 as compared to a previous imbalance of >1.5% O2.

In addition, the ability to control steam temperatures was not affected by the retrofit, and steam attemperation rates were virtually unchanged. This indicates that heat absorption patterns in the boiler were not substantially affected by the retrofit.

At equivalent loads the boiler is operating at 2 to 3 inches of water higher windbox pressure as compared to pre-modification operation. These higher levels are a consequence of more physical obstructions to flow with the PG-DRB burner and the PG piping in the windbox. In addition, the burner throat diameters were sized based on full load operation at 2% excess O2 or less. However, to control opacity to below 20%, excess O2 levels are commonly near 3% and this higher air flow rate through the dual registers of the PG-DRB burner results in increased pressure differential between the furnace and windbox.

The higher opacity with the new system continues to occur, and necessitates close operator attention to excess air, atomizer wear, fuel changes, and the degree of staging with overfire air during normal operation of the unit.

COST OF NOx CONTROL

The combustion system modification for Kahe 6 represents a total capital investment by HECO of over $3.9 million. A preliminary breakdown of these costs is as follows:

Process Capital -- materials, fabrication and erection costs for PG-DRB burners, ignitors, steam atomization, overfire air ports, windbox & ductwork modifications, firing system control modifications, and other misc. items	$2,775,000
Engineering -- HECO Production and Engineering labor, B&W engineering and flow modeling, and other outside engineering services	$880,000
Preproduction Costs -- outside start-up and testing services	$101,000
Inventory Capital -- spare parts	$7,000
Allowance For Funds During Construction -- interest paid on capital funding	$143,000
Total Capital Investment:	$3,906,000

These costs, equivalent to about $26/kW, are much higher than retrofit combustion control costs estimates generally reported in the literature. There are several reasons for this. First, the engineering and process capital costs are higher than might be normally assumed due to: (1) the decision to incorporate into the design a high degree of independent control and monitoring of combustion system parameters, (2) windbox and furnace flow modeling to support the system design, and (3) economy of size, 150 MW versus 500 MW for paper studies. Secondly, the retrofit was far from a simple replacement of existing equipment. As described above, the retrofit involved substantial ductwork and furnace water wall modifications to accommodate the new burners, PG flows, and OFA ports. The latter required separate runs of duct supplying hot air from the air heater directly to the OFA ports. Additionally, the new combustion system involved a conversion of the steam atomization system and a general upgrade of the Bailey firing control system. It should also be noted that since the unit was already equipped with an FGR system, the costs that would normally be incurred for the FGR fan and associated ductwork, controls, and secondary air mixing equipment were avoided. Finally, the shipping costs to Hawaii result in approximately 10% higher material costs than for a mainland site.

The differential operating costs for the new combustion system are currently being evaluated. Although the new system is not expected to result in higher net operating and maintenance costs, several factors in this regard are being evaluated: increased atomizing steam consumption for the new constant pressure differential system, increases in operating excess O_2, and potential changes in FD and FGR fan power consumption.

APPLICABILITY OF RESULTS TO OTHER BOILERS

This project has provided the utility industry and B&W with a better understanding of the retrofit cost, operational implications, and performance of integrated dual-register burner, overfire air, and FGR low-NOx combustion systems. Based on the Kahe retrofit experience and the test results, it can be reasonably concluded that this system is applicable to virtually all existing wall-fired utility boilers firing residual fuels. In light of the NOx/particulate trade-off, it appears that the ability to achieve desired NOx emission reductions with this technology will be especially sensitive to site specific factors such as fuel nitrogen, particulate formation tendencies of the oil, particulate/opacity regulations, and furnace O2 limitations. Since the NOx/particulate trade-off appears to be a generic feature of the technology (and may be relevant to other state-of-the-art combustion systems as well), more attention to oil atomization as a possible avenue for reducing particulate emissions is clearly warranted. In this regard an independent project funded by EPRI, ESEERCO, and Consolidated Edison Company of New York (Ref. 2) is in progress to develop a methodology to predict particulate emissions for a given fuel oil and boiler design, and to develop a design basis for improved oil atomization.

Costs for the PG-DRB system will vary, of course, depending on specific boiler design and level of NOx control required. It appears that the PG system is not effective and could be deleted from future designs, thereby avoiding its added complexity, costs, and associated impact on windbox pressure drop. It is also conceivable that FGR would not be required in some instances where NOx reductions less than the system's full capability are sought.

Finally, the design and engineering approach followed for this project -- involving flow modeling of critical flow distribution and mixing regions, flow calibration of individual components, and a high degree of independent control and monitoring of combustion parameters -- proved to be indispensable in optimizing and operating the combustion system. Such an approach is recommended for future retrofits.

CONCLUSIONS

Retrofit of the oil-fired PG-DRB system at Hawaiian Electric Company's Kahe 6 is the first application of this technology to a U. S. utility boiler. This project has significantly enhanced the U.S. utility industry's understanding of the performance and operation of this combustion system.

NOx and CO emissions were duplicative of the Japanese experience. However, it was necessary to push beyond the Japanese experience to simultaneously control NOx and particulate emissions. A trade-off between NOx and particulate emissions appears generic to the technology and is a major factor in system optimization. Further research to investigate better oil atomization to minimize particulate generation is recommended.

The NOx reduction goal of 0.23 lb/MBtu was achieved, notwithstanding the competing requirements for particulate and opacity compliance. The demonstrated NOx level of typically 0.2 lb/MBtu represents a 75% reduction from levels documented with the original burners when FGR was not used, a condition that might be representative of many uncontrolled boilers.

Overfire air (OFA) and flue gas recirculation (FGR) were dominant influences on NOx emission reductions with the PG-DRB system. Compared to the PG-DRB burners operating alone, OFA and FGR each further reduced NOx by about 50% and 30%, respectively. With combined operation of OFA and FGR, the reduction was nearly 60%.

Recirculated flue gas injected directly into the burner throat (designated "PG") was only marginally effective in reducing NOx, and is not likely to be justified for future retrofits.

The total retrofit cost of $26/kW reflects the relatively high complexity of the PG-DRB retrofit; engineering and design efforts to ensure integrated functioning of the burners, overfire air and flue gas recirculation systems; a high degree of adjustability of NOx control parameters to facilitate system optimization; the cost savings due to the use of an existing flue gas recirculation system; and somewhat higher shipping and installation costs for a Hawaiian site. This retrofit cost is higher and more realistic than estimates generally published for oil-fired boiler retrofit NOx combustion control.

ACKNOWLEDGMENTS

The authors wish to thank Babcock & Wilcox for providing test equipment for the HECO/EPRI tests. Additionally, the cooperation and advice from the Kahe Station operating and maintenance personnel during the test program is gratefully acknowledged.

REFERENCES

1. A. LaRue and P. Cioffi, "NOx Control Update - 1987." Proceedings of the 1987 Symposium on Stationary Combustion Nitrogen Oxide Control, Vol.1, EPRI CS-5361, August 1987.

2. ESEERCO Research Project EP85-15: "Heavy Oil Combustion", sponsored by the Empire State Electric Energy Research Corporation (ESEERCO), Consolidated Edison Company of New York, and EPRI. (in progress)

Table 1

KAHE 6 FUEL OIL ANALYSES

	Range for Baseline	Typical for Post-Retrofit
Composition (%Wt):		
Carbon	86.2-87.4	87.6
Hydrogen	6.3-11.6	11.3
Nitrogen	0.20-0.46	0.31
Sulfur	0.34-0.47	0.43
Ash	0.01-0.03	0.02
Oxygen, by difference	1.4-5.4	--
Conradson Carbon (%Wt)	7.6-10.3	6.7
Asphaltene (%Wt)	1.7-3.2	1.3
Pour Point (degrees F)	95-110	--
API Gravity (@60 F)	13-20	17
HHV (Btu/lb)	18560-19070	18860

Reproduced from
best available copy.

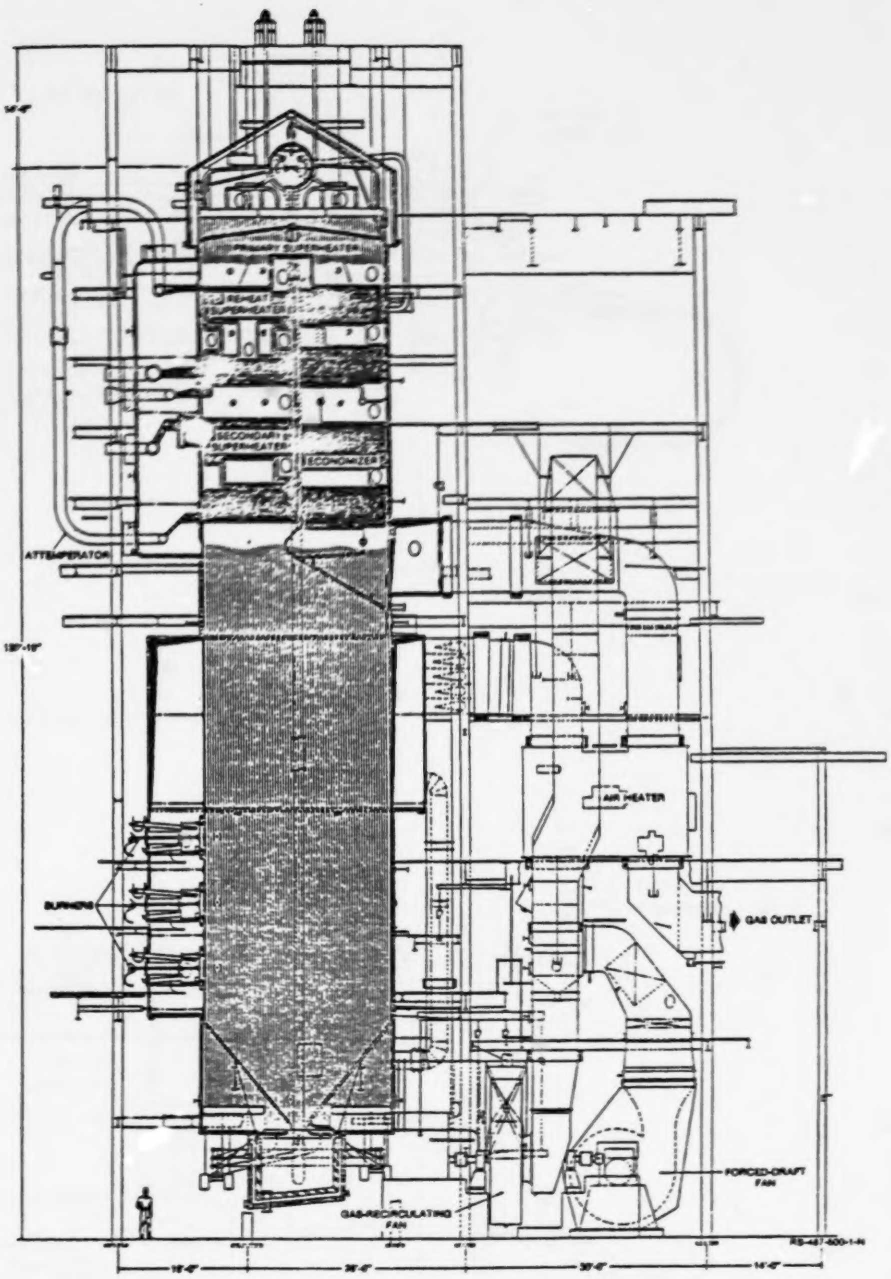


Figure 1. Kahe Unit #6 Elevation Drawing

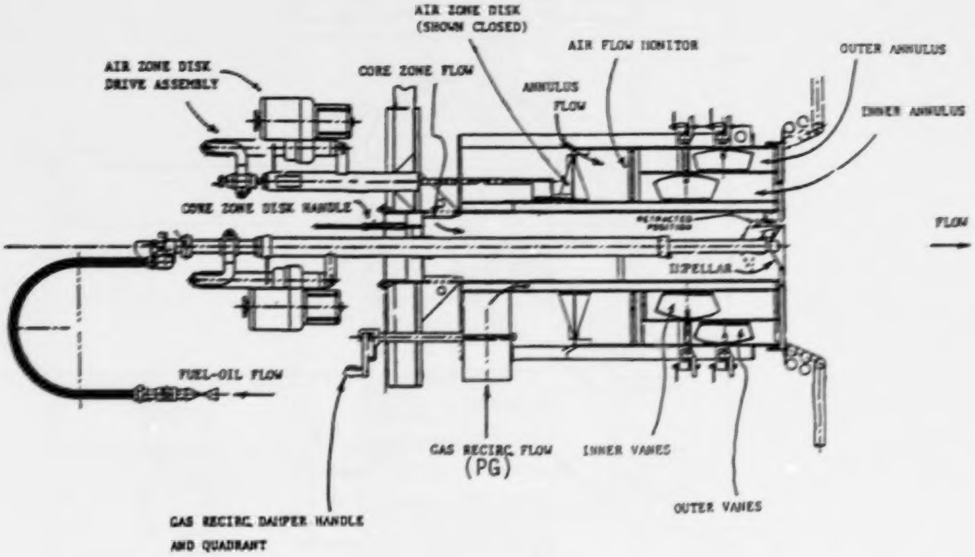


Figure 2. Babcock & Wilcox PG-DRB Burner

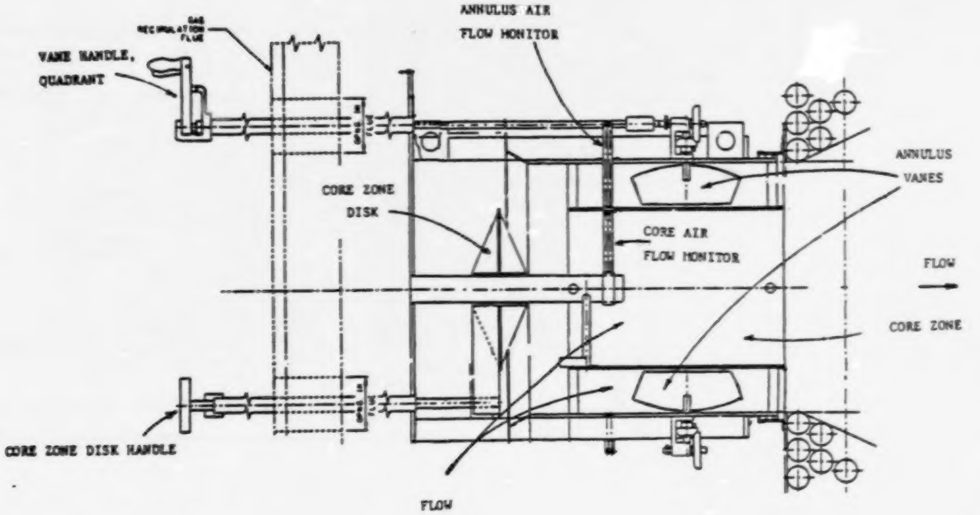


Figure 3. Overfire Air Port with Velocity Controlled Throat

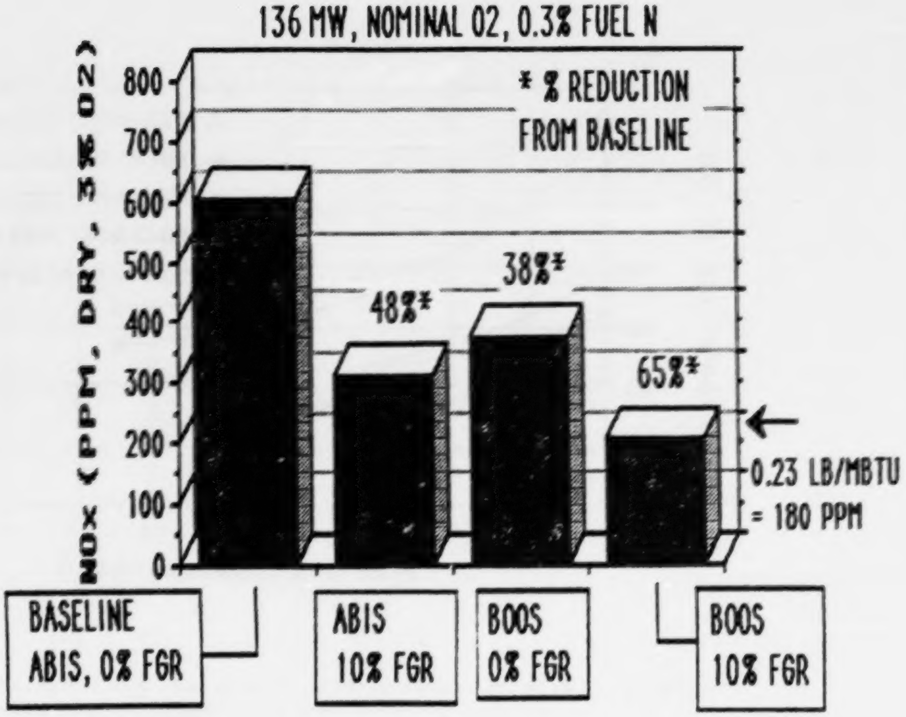


Figure 4. Pre-retrofit "Baseline" NOx Summary

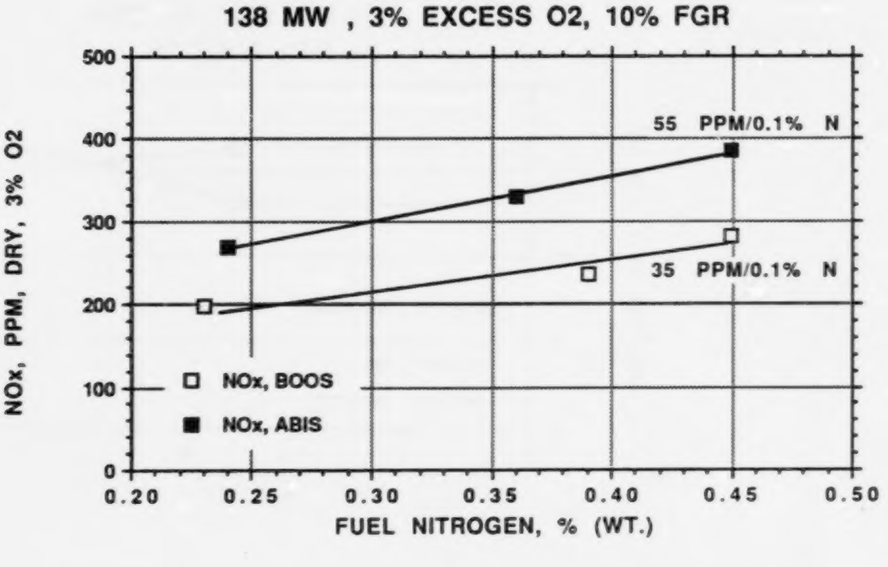


Figure 5. NOx Dependence on Fuel Nitrogen Content

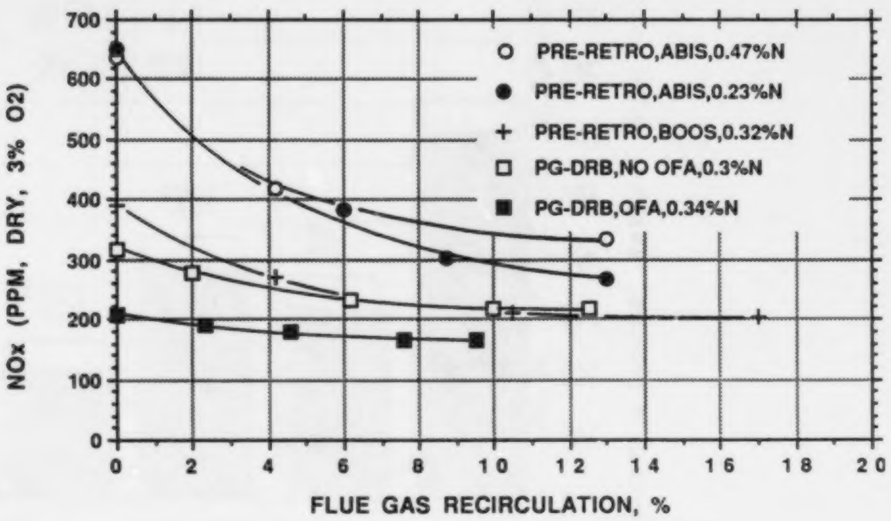


Figure 6. Effectiveness of FGR in Reducing NOx Emissions, Comparing Baseline and Post-retrofit Operation

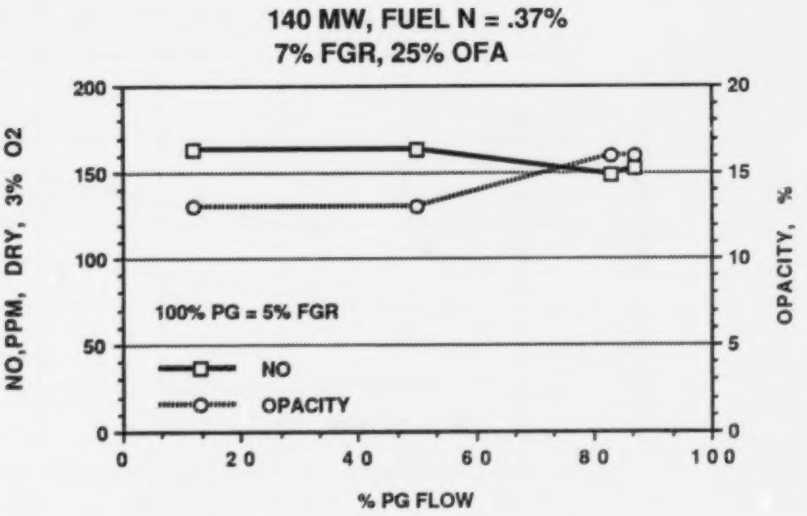


Figure 7. Effect of PG Rate on NOx

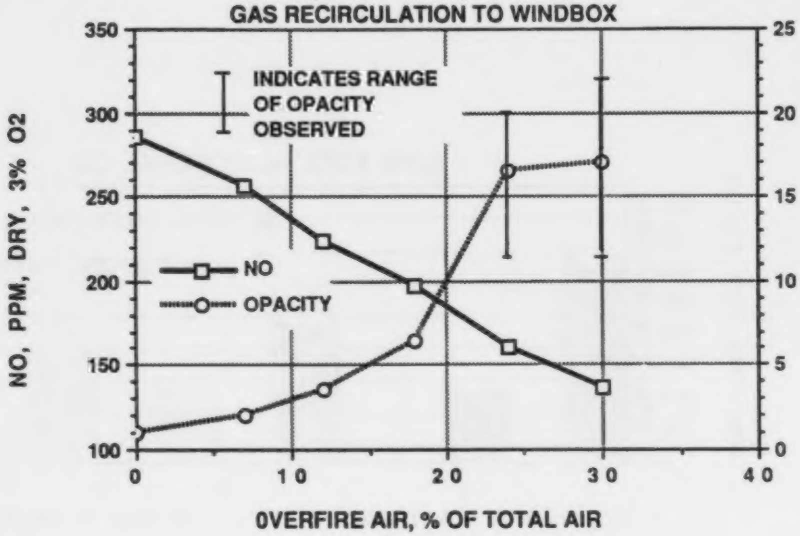


Figure 8. Effect of OFA on NOx and Opacity

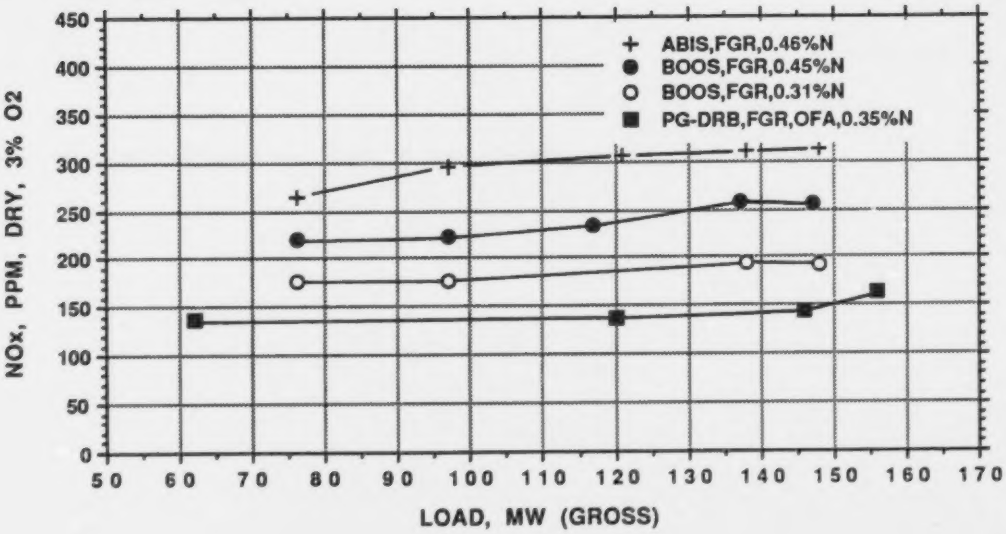


Figure 9. NOx versus Boiler Load for Baseline and Post-retrofit Operation

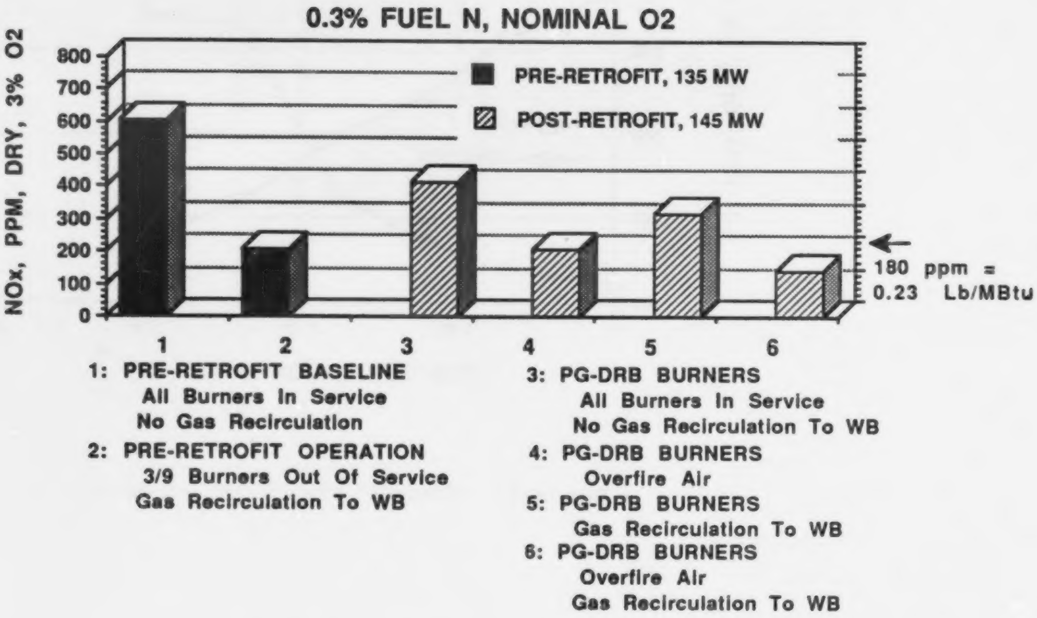


Figure 10. Summary Comparison of Baseline and Post-retrofit NOx Emissions

GAS URBINE NITROGEN OXIDE (NOx) CONTROL
CURREN TECHNOLOGIES AND OPERATING EXPERIENCES

Leonard Angello
ectric Power Research Institute
3412 Hillview Avenue
Palo Alto, CA 94303

Phillip Lowe
InTech, Incorporated
11316 Rouen Drive
Potomac, MD 20854

ABSTRACT

National standards for NC control for gas turbines are being evaluated and modified throughout the w ld. These standards are often supplemented by local or site specific emission li ts. Specific allowable emission levels range from about 10 to 120 ppm (part per million, volume basis) in the U.S., depending upon the capacity and efficier of the gas turbine application and the local environmental needs for NOx cont l. In response to those requirements, the equipment manufacturers and plant c rators have designed and installed one or combinations of four control technolog s: fuel switching; wet combustion controls; dry combustion controls; and exh st gas treatment. In addition, catalytic combustion control systems are prese ly under development but are not commercially significant at this time.

This paper presents a bri overview of the national NOx emission requirements of Europe, Japan, and the Un ed States. A description of the control processes presently being applied a commercial facilities is provided and typical operating results and experiences a also presented. Differences between the operating results and design condit ns are highlighted. The advantages and disadvantages of each control technolog are summarized, and areas or topics of uncertainty or high risk that could bene t from additional research are identified.

In this paper, all NOx va es are referenced to dry, 15% oxygen exhaust conditions unless otherwise stated. he units are volumetric, in parts per million (ppm) unless otherwise stated.

Presented at the 1989 JOI SYMPOSIUM ON STATIONARY COMBUSTION NOx CONTROL, March 6-9, 1989, San Fran sco, California.

INTRODUCTION

When gas turbine power generation first entered the electric utility market it was hailed as a clean, benign source of power. There were no giant cooling towers to dominate the landscape; no coal delivery or ash removal; noise could be effectively screened by suitable acoustic enclosures; and stack emissions were barely visible.

Today, over 25 years later, the 140 MW unit with a turbine inlet temperature approaching 2300°F is a reality. The inherently high potential for exhaust heat recovery, and the greater efficiency of the combined cycle has insured a role for the gas turbine in power production programs around the world.

But in parallel with this trend there has developed a growing awareness of the need to protect the environment. As gas turbine operating temperatures have risen to provide greater output and efficiency, equipment manufacturers and plant operators are confronted with increasingly strict air quality control standards - particularly in regard to oxides of nitrogen (NOx).

NITROGEN OXIDE (NOx) EMISSIONS AND STANDARDS

The major component of NOx is nitric oxide (NO) formed by oxidation of atmospheric nitrogen at high temperatures. The reaction has been shown to be exponentially dependent on temperature and linearly dependent of time. It has become an increasing problem for designers with the introduction on new models with turbine inlet temperatures over 1850°F.

Between 850°F and 1200°F the NO can be oxidized to NO_2, a brown gas which can be highly visible at part-load unless steps are taken to inhibit this reaction. Together these two oxides of nitrogen are the principal components of NOx.

NOx forms in two ways. First, fuel-bound nitrogen can be present as a chemical component of the fuel molecules. This reacts with combustin air as the fuel is burned. The amount of NOx produced depends on the nitrogen content of the fuel.

Thermal NOx, on the other hand, is produced by oxidation of atmospheric nitrogen at high firing temperatures. Concern about NOx emissions has mounted with the increase in firing temperatures and suppressing the formation of these gases is an important facet of current gas turbine research.

Fuel type (natural gas or distillate fuel oil) as well as the fuel nitrogen content has a major impact on NOx emissions. This is mainly due to the difference in flame intensity (adabatic flame temperature) which different fuel produce when they are burned.

Figure 1 illustrates the affect that fuel type and firing temperature have on uncontrolled gas turbine NOx emissions. As shown, uncontrolled NOx emission range from 90 to 140 ppm for a typical heavy-duty gas turbine fired by natural gas over the range of firing temperatures between 1800 to 2100°F. The same unit fired with distillate fuel oil produces NOx emission of 140 to 210 ppm over the same range of turbine inlet temperatures.

In the U.S., the requirement to control NOx and the limitations or emission levels that must be achieved are presented in Federal and state regulations, with the more severe requirements taking precedence. Thus, both requirements must be examined for applicability.

Table 1 presents a summary of selected national emission standards for NOx, expressed as NO_2. The table shows that the U.S. has the most-stringent national standards for the industrialized countries examined.

Table 1

SELECTED NATIONAL NOX EMISSION STANDARDS
(For Application to Gas Turbine Facilities)

Country	Turbine Capacity, MWe	Emission Limits, ppm	Emission Limits, mg/Nm^3
FRG	60 & larger	147	300
	less than 60	172	350
US	10 & larger	75	153
Japan (Natural gas)	10 & larger	100	205

In addition to the national emission standards, local government authorities can and do impose more stringent standards. In the U.S., for example, national standards require something in the range of 75-140 ppm for electric utility gas turbine emissions, depending upon the plant efficiency and fuel nitrogen content as shown in Figure 2. However, several local authorities in California have imposed standards for application to the smaller turbines used in cogeneration facilities, ranging from 15-42 ppm (some recent cogeneration facilities in California have actually been permitted at 4.5 ppm), reflecting those regulators' understanding of the lowest achievable emissions rate (LAER) controls available.

As stated earlier, the type of fuel that is fired strongly impacts the NOx emissions, and the emission standards generally recognized this fact. Table 2 presents a comparison of the emission limits for oil and gas-firing, for selected countries.

Table 2

EMISSION LIMITS COMPARISON
FOR OIL AND GAS-FIRING

Country	Ratio of Emissions Limits Oil-Firing	Ratio of Emissions Limits Gas-Firing
Austria	1	0.79
Canada	1	0.67
FRG (after 1984)	1	0.67
Japan (after 1987)	1	0.46
Switzerland	1	0.56
U.S.	1	0.67
ECC (proposed up to 1995)	1	0.79

The numeric value of any emission limit is also directly influenced by the actual NOx removal capacity of the specific technologies that can be applied to the processes and equipment that will be governed by the emission standards. That is, emission limits can not be so restrictive that there is no technology available that can be applied to meet the permit condition. However, as new technologies are developed to meet the ever increasingly restictive emission limitations. They become the standard by which the next round of emission limits setting is guided.

Current NOx control technologies for gas turbine applications employ fuel switching wet combustion control (steam or water injection into the combustor), or exhaust gas treatment (selective catalytic reduction technology) or combinations of those controls.

Recently, dry combustion controls have been, or are being commercially, developed by the gas turbine manufacturers, and catalytic combustion control processes are being research. Each of these NOx control technologies is discussed in following sections.

FUEL SWITCHING

The simplest way to reduce NOx is to reduce the nitrogen available for converstion into NOx. Natural gas-firing will produce about two-thirds of the NOx that firing with a light distillate oil will. Since the uncontrolled NOx emission from natural gas-firing will not, in general, meet current emission limts, additional controls are required. This imposes the restriction that the subsequent control technology must be compatible with the fuel. For example, high sulfur bearing or fuels with alkali or arsnic compounds can poison the catalysts used in the selective catalytic reduction (SCR) process. Thus, if that approach were to be used, it would impose some constraints on the choice for fuel switching.

WET COMBUSTION CONTROLS

This is perhaps the most widely used, commercially available NOx control technology. NOx reductions of up to 80% compared to the uncontrolled system are possible. Steam or water is injected into the combustion chamber at ratios of fluid to fuel of up to 2.4 (by weight), although most systems have a practical limit of injection ratios of 1.0 or less. The fluid reduces the combustion intensity and temperature. When water is injected part of the fuel energy is used to vaporize the water, which lowers the combustion intensity. Thus, water is more effective than steam, on a weight basis. However, it can lead to more erosion and wear problems.

Additional fuel can be burned to counter the heat of vaporization effects, and the turbine power output increases because of the additional mass throughput which comes from the water flow. As the amount of water injection increases, the level of unburned hydrocarbon and carbon monoxide emissions increase. Figure 3 gives a typical example of the increase in CO as NOx is reduced. As the NOx control is pushed to yield large percentage NOx reductions, significant CO and unburned hydrocarbon (UHC) emissions can result, requiring the installation of additional controls for those pollutants. These controls are often based upon the use of catalysts and are very sensitive to temperature conditions. This in turn can impose strict limits on the part load operation of the gas turbine. A major disadvantage of the wet combustion control processes is the cost associated with the supply of the water or steam, and in some cases, the actual availability of the water or steam itself. The technical problems with fluid injection include internal pressure fluctuations which increases in component erosion and wear. Impurities in the fluid, especially in water, can significantly effect turbine blade wear and erosion. The durability of liners and transition pieces have also been impacted. Wet systems can yield 30 - 75 ppm NOx emissions for gas firing and

50 - 150 ppm for oil firing. Considering the point of share increase in CO emission as shown in Figure 3, and the erosion and wear problems that occur with water (or steam) injection, 40 ppm appears to be a practicable lower limit for manufacturers to meet for gas firing and still warrant their equipment (although some advertise the ability to achieve even greater control levels). Fifty to sixty ppm would be the corresponding lower limit for distillate fuels.

The technical performance of wet combustion controls can be represented by data similar to that given in Figures 4, 5 and 6. Figure 4 shows the NOx reduction achievable as a function of the water injected into the combustor, expressed as the ratio of the amount of Water to Fuel injected, on a mass basis. Similar curves (Figure 5) can be anticipated for other turbines or for steam injection. The data shows that between 60-80% NOx reduction (expressed as an R factor of 0.4 to 0.2 in Figure 4) is possible. For reductions much above 70% it can be seen that the CO and UHC emission increase as such a rapid rate that an oxidizing catalyst is usually be required to control those emissions.

Injecting water into the combustor increases the power output of the engine. This is a function of the increased mass flow through The turbine if the fuel/air ratio is maintained. The heat of vaporization of the water is lost, this results in increased fuel requirements if operation is held to a constant cycle temperature. Figure 6 shows this impact for one turbine supplier. At a water to fuel injection ratio of 0.8 the curve shows that 8% more fuel is required to maintain the turbine output temperature. At that condition, 6% more power output is achievable from the engine.

The water injection system will include manifolds to control the water flow and to assure that water can not flow back into the fuel or air injection system. As the control point is moved to more and more NOx reduction, the control of the amount of water flow, compared to the fuel flow, becomes critical. Very accurate flow metering is required and very tight control on the water purity is also required in order to eliminate or reduce erosion or wear problems. Some problems that have occurred are nozzle clogging and corrosion, pressure fluctuations and wear due to imbalances in water flow to specific nozzles within the combustor, and high temperature differentials and flame instability, which also can lead to combustor or turbine component wear and erosion problems. The water quality specification should control particulate matter as well dissolved chemicals and the pH of the water supplied.

A summary of the disadvantages of this method of NOx control is that it will increase the emissions of carbon monoxide and unburned hydrocarbons (and perhaps require the use of an oxidizing catalyst for pollution control for these items), it will increase the fuel consumption from 1 to 4% (or a decrease in the net power output), the system capital costs and operating costs will increase, the engine control and monitoring system complexity will increase, the control system will require a large supply of water that can not be recovered (it is discharged as steam from the exhaust stack), and the engine durability may decrease while the system overhaul frequency increases.

DRY COMBUSTION CONTROLS

This is a commercially available NOx control technology for some of the turbine suppliers; it is under development at others. Dry combustion controls show the promise of significant cost reductions compared to wet combustion controls, and perhaps a slight improvement in the magnitude of the control is also possible. NOx reductions of up to about 60% have been achieved, and in special instances reductions of over 80% have been reported (e.g. NOx discharges of 30 ppm). These technologies are based upon reducing the flame turbulence and intensity, enhancing the fuel/air mixing, and establishing fuel lean zones within the combustor. They generally rely on a staged combustion with the first stage used as a pilot burner followed by a secondary stage of multiple fuel injection nozzles. The second stage often employs burning a lean, premixed fuel/air mixture in order to assure a uniform mixture and the avoidance of high temperature regions in the combustor. Obtaining the uniform mixing is very important in achieving this goal.

The control of the two burner zones and the preparation and control of premix air complicates the combustor control and often requires the use of sophisticated mechanical control systems. The pilot or first burner is generally used to start up and carry the initial engine load. The control system can be based upon using variable geometry, variable air flow scheduling, or combinations thereof. At higher loads the second stage picks up the load and the first stage is used to provide preheat to the second stage. Figures 7 indicate how one supplier's control system works. In Figure 7 the step change in the NOx level indicates when the engine control was changed from relying on the first stage nozzle in the combustor to the set of second stage nozzles. However, it also shows that the CO limit could easily reach 500 ppm or larger, as the engine may have a very limited operating region between having high NOx-low CO or high CO-low NOx emissions. Manufacturers who use external silo-type combustors can more easily adapt their designs to different sized turbine application than can those who use internal combustors. A clear advantage of the dry control system is the elimination of the costs of providing large quantities of clean water. But the impact of the dry controls on component wear and erosion and the engine durability have not yet been demonstrated by large numbers of operating hours under U.S. utility operating conditions. This remains an area of significant technical uncertainty, and reliability testing in a field application will be a very important part of establishing the actual reliability of these systems.

The technical performance of the dry combustion modification NOx controls is much more a function of the manufacturer's equipment than is the corresponding performance of wet controls. Thus, although Figure 4, 5 and 6 are typical of the wet controls in general, the data of Figures 7 and 8 are really only representative of the performance of one specific equipment supplier's dry, low NOx (DLNOx) system. However, they are illustrative of the performance range possible for dry controls. As indicated earlier, the dry controls usually have two stages of combustion, and the NOx control performance has a step change in the NOx emissions as the turbine load being carried is shifted from stage one to stage two. In Japan, the turbine NOx emission typically is set at about 75 ppm, apparently on the basis that an 80% efficient SCR control system also will be required. This combustion of combustion control and exhaust gas treatment will yield a 15 ppm stack emission, thus tighter combustion controls are not needed. The actual achievable control limit for the dry control technology could be less than 75 ppm, but plant operating data to support a commercial decision to operate at lower NOx emissions is not yet available. It is also noted that some U.S. and German turbine suppliers have indicated that they may be able to achieve NOx emissions as low as 30 ppm. Supporting data will be very important in evaluating these claims. Also, the Japanese data show that the combustor control settings are critical with respect to the emission of significant amounts of CO. The UHC emissions are unreported, however, experience indicates that they follow the same trend as the CO emissions. Hence, a report on very low levels of NOx emission needs to be evaluated in the context of how that operational condition impacts CO and UHC emissions.

The Japanese experience is that the combustion control needed to transfer load between burner stages (e.g. to transfer from low to high load) is difficult to achieve. Figures 7 and 8 show a step change with the NOx emissions at the load transfer point, indicating a step change in combustion conditions. Step changes are, in general, not desirable from the point of view of engine stability and durability. In one Japanese design a mechanical setting for bypass air flow is required. Although it is stated that the control can be made while the system is on line, reported plant startup problems suggest that establishing the control setting is difficult. Also, that manufacturer is developing "improved" dry controls, further indicating that the operation of the present control system is difficult. It is noted that the ambient air condition can effect the control system performance, and a 15 degree change in local temperatures can result in a requirement to adjust the bypass air control setting. These conditions may have helped contribute to the Japanese decision to operate the turbines at 75% of full load or higher, severely limiting load following capabilities.

In general, the turbine suppliers of dry NOx controls have not supplied data on CO and UHC emissions, but it appears that they are operating the turbine in a manner such that additional CO and UHC emission controls are not necessary (see Figures 7). One advantage of the dry control technology is the lack of the requirement for additional diluent (e.g. water or steam) preparation and control facilities. It may, however, be quite difficult to obtain a warranty and have the resultant ability to operate the turbine on a backup or emergency liquid fuel, since the dry combustion controls may not be able to accommodate the burning characteristics of those distillate fuels. Finally, long term reliability of the control process and its long term impact on other engine components need to be established.

CATALYTIC COMBUSTION

This NOx control approach is not commercially available for combustors of a physical size of general interest. Estimates of the remaining development time range from 5 to 10 years. Small combustors are available, and larger combustors have been tested in laboratories. In some of those tests very low emissions, as low as 1 to 5 ppm, have been reported; but in general higher emissions result when the combustor is operated to obtain the high efficiencies needed for a gas turbine applications. In actual application, the catalytic material is often placed upon a substrate material such as a ceramic material. Pilot burners are used to preheat the fuel/air mixture to the initial reaction temperature. Catalytic combustion can produce combustor exit temperatures in the range of 2000°F, suitable for further conditioning for gas turbine use. The major problems that have been experienced deal with sealing the catalytic section against the combustor shroud and in developing a rugged, durable catalytic section. Physical failures such as cracks and the subsequent breakup of the combustor frequently have been observed. Development needs to focus on producing durable combustors as well as controlling the combustion over an appreciable operating range.

EXHAUST GAS TREATMENT (Selective Catalytic Reduction (SCR))

There are control methods available and under development that treat the NOx in the turbine exhaust gas to remove it. Under certain conditions reductions of NOx of about 90% are possible, compared to the uncontrolled case. These methods can be used independently or in conjunction with combustion modification controls. Japan has been very active, compared to the U.S., in applying some of these controls; but recent experience in Germany and earlier experiences in the U.S. in coal-fired plants indicate that the technology must be modified if it is to be successfully applied in U.S. operating systems and with U.S. operating philosophies.

Ammonia can be used as a reducing agent to react with nitrogen oxides and oxygen to produce nitrogen and water. Catalysts are used to promote the reaction at lower temperatures. A series of titanium and vanadium oxide catalysts on metal or ceramic substrates have been used extensively in Japanese utility facilities (and other industrial facilities) to reduce NOx emissions. The catalysts are formulated to optimize the conversion in the temperature range of 570 to 850°F, with most operations focused near the 700°F temperature range. It takes one mole of ammonia to reduce one mole of nitrogen oxide and two moles of ammonia to reduce one mole of nitrogen dioxide. In commercial practice the catalyst is designed to reduce 80 to 90 percent of the NOx emissions for ammonia injections, on a mole ratio, equal to the amount of NOx present for the exhaust gas. In some cases it has been advertised that the system was designed for 95% NOx removal. In Japan the operational practice (as contrasted to design conditions) is to operate the system with reduced ammonia injection (reduced from the design injection amount). This results in a NOx removal rate of 60 to 75% with a corresponding bypass of ammonia that passes through the reactor without reacting with the NOx, thus slipping past the reactor and resulting as a low level pollutant emission.

The Japanese also design their SCR systems for a space velocity (the volumetric gas flow divided by the catalyst volume) for gas-fired systems of about 4,000 to 10,000/hour (with a pressure drop of about 4 - 6 inches of water), with some development being directed towards expanding that value to about 20,000/hour. The reasons for the Japanese operational approach are varied. They appear to be a result of their desire to limit ammonia emissions; a recognition of the difficulty of controlling the system at the design condition; a recognition of the difficulty of reliability measuring NOx and ammonia at the very small ppm operating conditions; a recognition that such an operational strategy appears to materially increase the durability and operational life of the catalyst and NOx reduction system equipment (a key factor in controlling system costs); and a recognition that such operations reduce the problem in introducing ammonium sulfate and bisulfate salts into the exhaust stream when fuels that contain small amounts of sulfur are fired in the turbine. Most SCR applications in Japan are applied in concert with some form of combustion modification NOx control.

In the U.S. there is less electric utility experience, and no gas turbine electric utility experience with SCR NOx control. However, several cogenerators (mostly in California) are using the control technology in conjunction with water or steam injection combustion modifications for a total NOx control system designed to limit the NOx exhaust emission to 8 to 15 ppm. The space velocity of the U.S. systems has been on the order of 30,000/hour (with a pressure drop of 2 - 4 inches of water), with tests performed on systems with space velocities of up to 100,000/hour. In the U.S. the systems have been designed for an ammonia slip of 20 ppm or larger at ammonia to NOx injection ratios of about 1.0, and the systems are operated for "90% or higher" NOx removal. Operating data is not readily shared, so this high performance condition is not easily verified. There have been mixed results with the new U.S. applications, several have come online without apparent problems, others have had required extensive shakedown periods and do not appear to be operating as designed. Problems mentioned (but not reported with any significant detail or with the release of experimental evidence) include: the life and availability of the SCR catalyst itself; ammonia consumption; ammonia injection controls and monitoring instrumentation; and plant operations, especially at throttled conditions. It will take time to establish the long term system reliability and availability and its impact on plant economics.

In any SCR system the system operational temperature range is below the turbine exhaust temperature, which is around 1000 - 1100°F. The SCR system is installed in the heat recovery steam generator. The exact location is dependent upon whether the steam generator has auxiliary firing (or if duct firing is employed) to increase the plant output. The SCR catalyst is usually located somewhere after the superheater and before the economizer tubing. In small cogeneration systems the ammonia injection, and hence the SCR operation, is terminated at part power operation whenever the gas temperature entering the SCR reactor falls below that required for efficient operation of the reactor. To continue operations at such low temperatures would introduce excessive ammonia emissions into the exhaust gas. In a large utility system it may be desirable to include physical arrangements for bypassing the superheater in order to operate the SCR at lower plant power levels. Such is the case for fired boiler operations in some Japanese systems. Because of the higher levels of ammonia bypass in the U.S. systems, great care must be exercised when sulfur bearing fuels are burned in the combustor or the ammonium salts will be formed. One U.S. cogenerators has already experienced problems because of the formation of ammonium bisulfate salts on downstream equipment and the poisoning of the catalyst by the sulfur compounds in the exhaust gas.

The SCR reactor also oxidizes sulfur dioxide to sulfur trioxide. This is another cause for limiting the sulfur content in the fuel. The ultimate disposal of the spent catalyst needs to be considered, since it contains heavy metals and is classified as a hazardous waste material. In Japan the catalysts for gas turbine operation have been used for 4 to 7 years. In the U.S. they are being offered with lifetime warrantees of 1 to 2 years.

Other problems that have occured in operating SCR systems include operational problems with the ammonia injection system and the control and monitoring instrumentation. The specification of the measurement instrumentation is still an open question. In Japan the use of chemiluminescence-based instruments have been discontinued in favor of the use of infrared-based instrumentation, and ultraviolet absorption-based instruments are under development. The chemiluminescence-based instruments are still used in the U.S.

SUMMARY

The commercial status of gas turbine NOx controls to a large degree, will impact the further development and demonstration of improved technologies. Wet combustion control is commercially available and technically established. But cost, its impact upon turbine wear and erosion and regulatory requirements of lower NOx emission levels is causing this to become a less desirable technical solution for NOx control.

Selective catalytic reduction technology is currently established in the commercial market place. Technical issues persist, and the costs may therefore be larger than those presently expected. Its use appears to be allocated for those situations where the combustion control technology is insufficient to reach the regulated NOx emissions limits. In those cases it is used in addition to the combustion control technology. It has not been applied as a stand-alone NOx control system at a gas turbine facility, probably a further indication that it is an expensive control system and that the control system reliability and its effect upon the power generation system availability are not established at a confidence level necessary to promote rapid commercial expansion of the technology. EPRI has an ongoing research program that will evaluate the performance and reliability of existing SCR/gas turbine systems.

Dry, low NOx combustion control is just entering the market place. It shows the promise to be effective or even more effective as than wet NOx combustion control. Questions remain as to its ability to allow load following operations, and its use may also require additional CO and UHC controls when very low NOx emission levels are required. Because of its newness in the market place, there is not sufficient information available to comment on the long term reliability of the control system and its subsequent impacts on the rest of the engine. However, EPRI anticipates developing a program of field tests to evaluate several of these systems in actual utility settings.

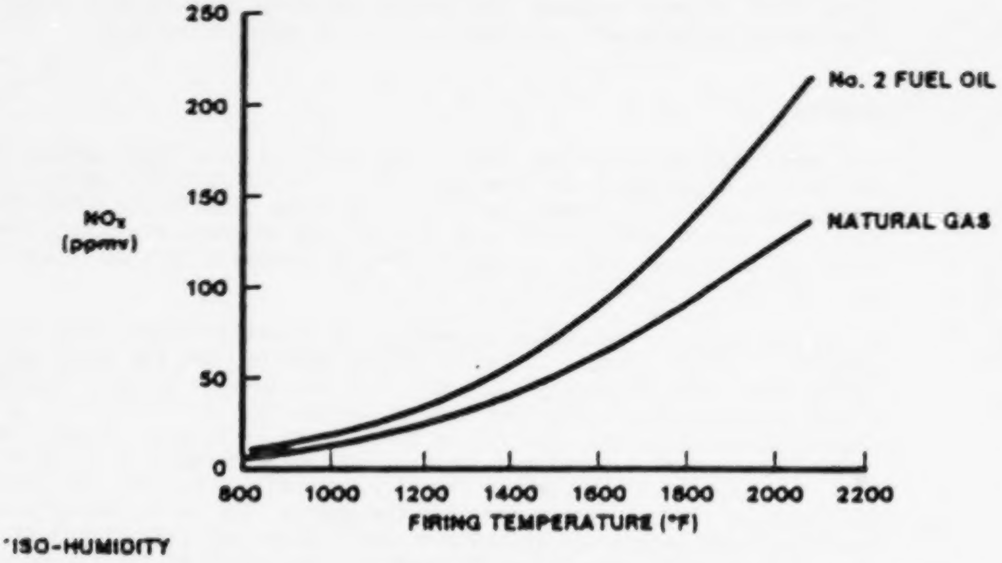
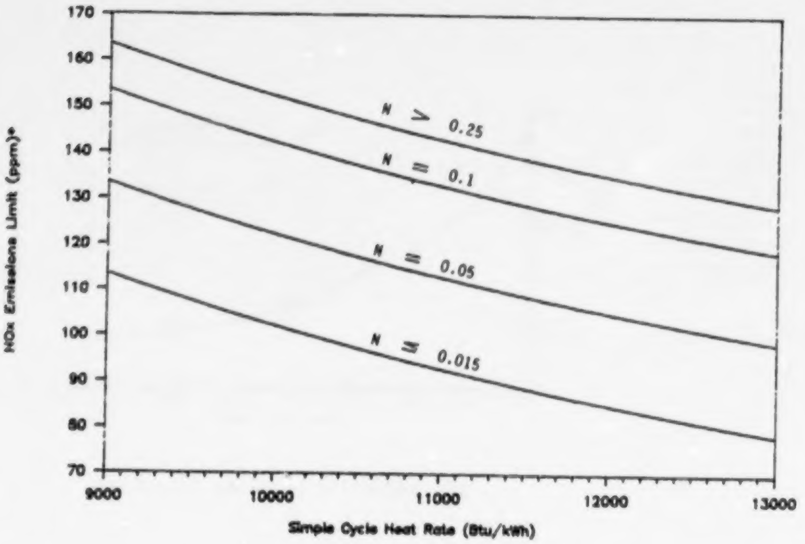


Figure 1. Effect of fuel type and firing temperature on uncontrolled NOx emission for a typical heavy-duty gas turbine.



* at 15% oxygen, on a dry basis

Figure 2. New source performance standard limits for nitrogen oxide as a function of simple cycle heat rate and fuel-bound nitrogen content.

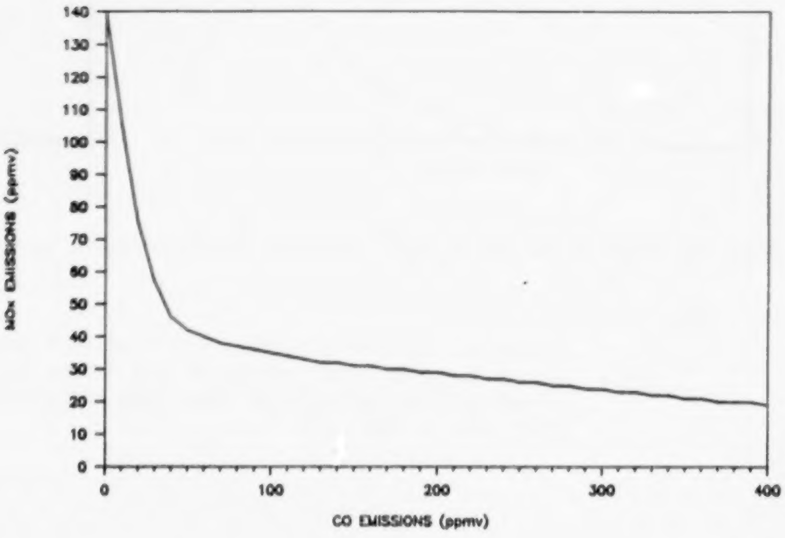
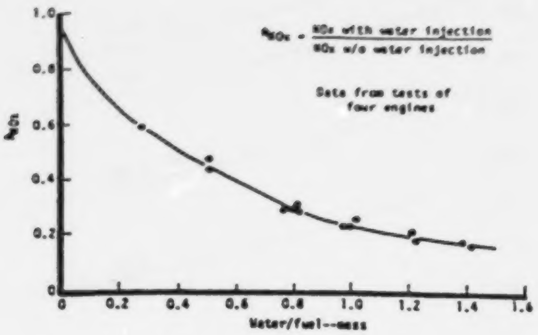
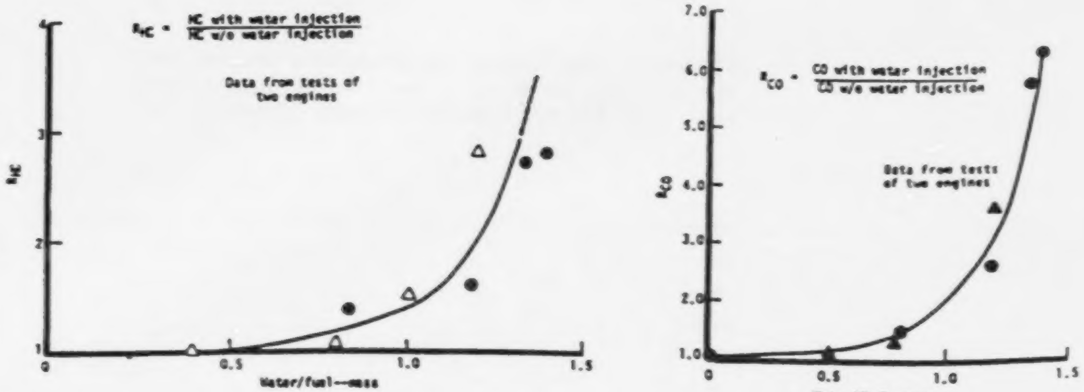


Figure 3. Relationship between nitrogen oxides and carbon monoxide emissions.



. NOx reduction by water injection



Increase in hydrocarbons due to water injection Carbon monoxide increase due to water injection

Figure 4. Effect of water injection rate on nitrogen oxide carbon monoxide and hydrocarbon emissions for gas turbine base load operation with natural gas.

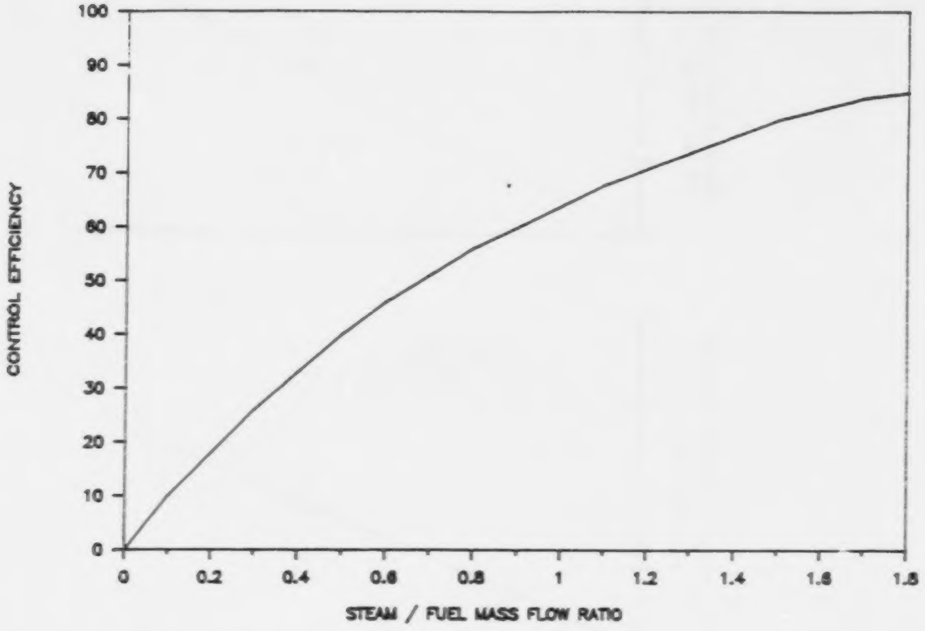


Figure 5. Effect of steam injection rate on NOx control efficiency.

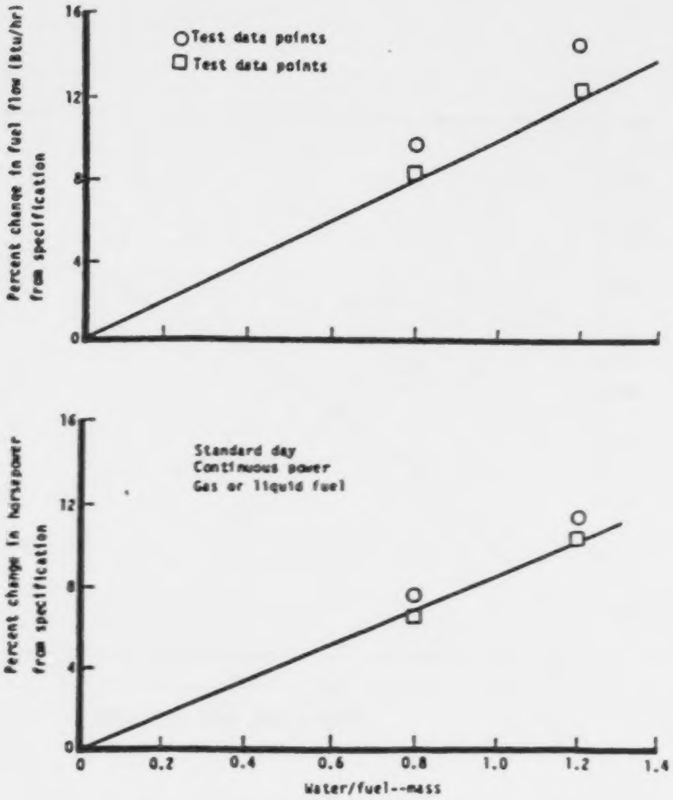


Figure 6. Effect of water injection rate
o gas turbine performance.

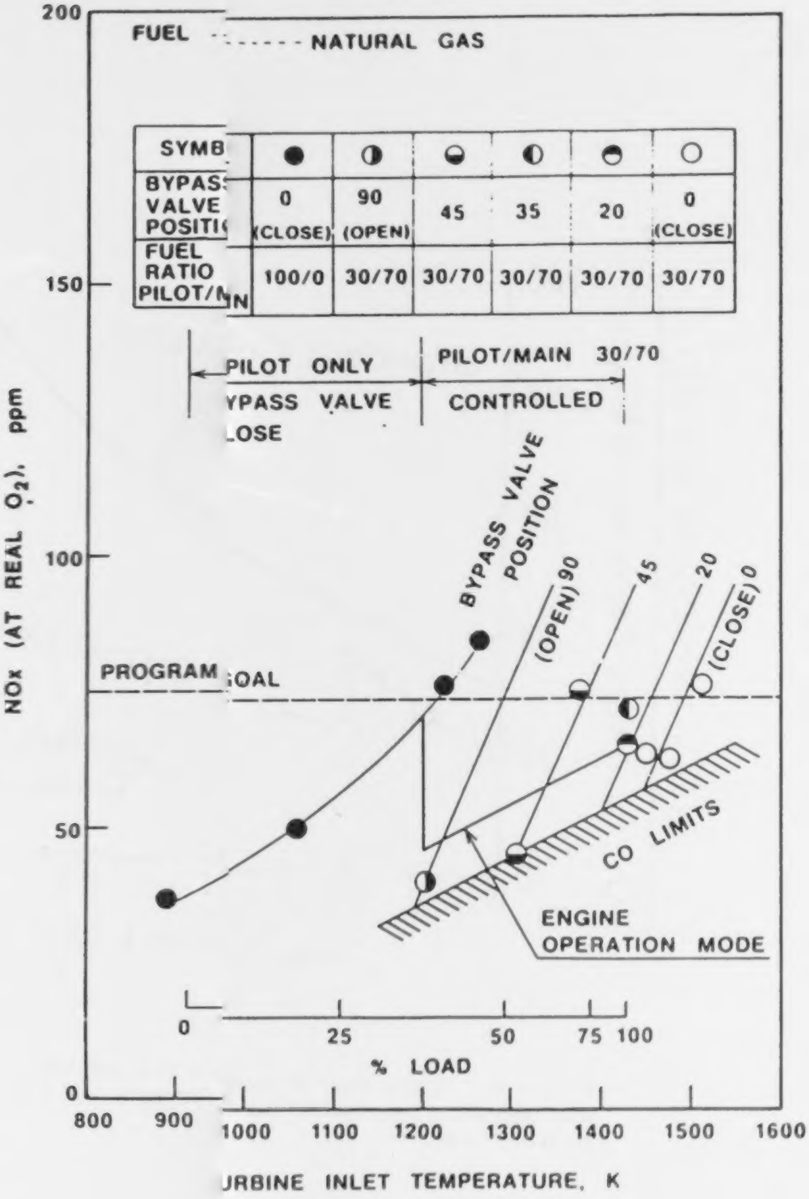


Figure 7. Dry low NOx (DLNOx combustor emission characteristics.

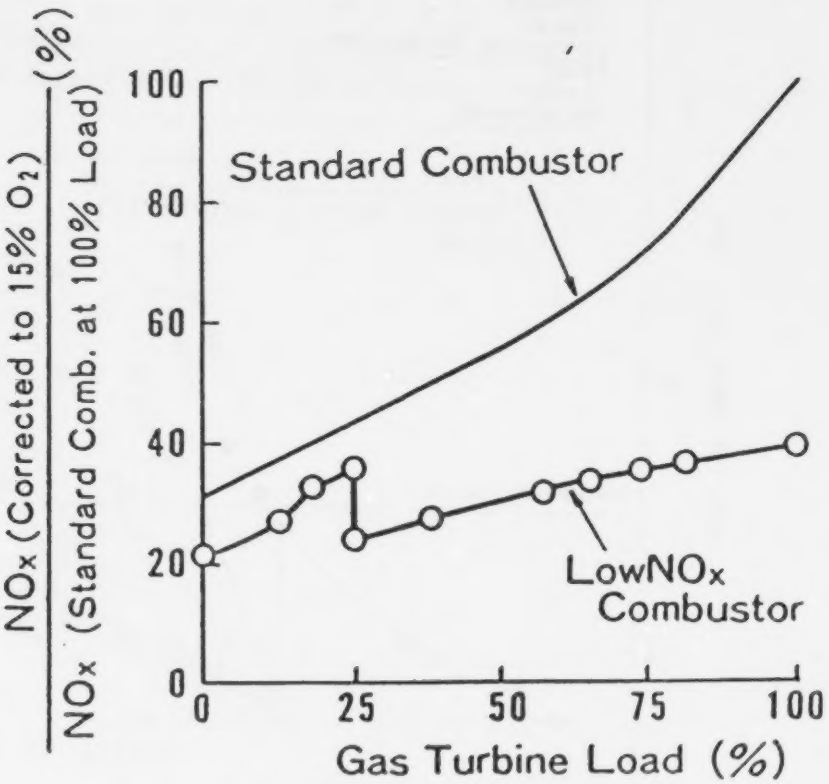


Figure 8. Comparison of standard and dry low NOx combustor NOx emissions performance vs. gas turbine load.

DEMONSTRATION OF AN AUTOMATED UREA INJECTION SYSTEM AT ENCINA UNIT 2

JAMES H. NYLANDER
SAN DIEGO GAS AND ELECTRIC COMPANY
POST OFFICE BOX 1831
SAN DIEGO, CALIFORNIA 92112
AND
M.N. MANSOUR AND DOUGLAS R. BROWN
APPLIED UTILITY SYSTEMS, INC.
1140 EAST CHESTNUT AVENUE
SANTA ANA, CALIFORNIA 92701

ABSTRACT

The design of an automated urea injection system that can follow changes in boiler load under load dispatch is discussed. The effect of urea injector design on NO_x removal is presented. Parameters influencing NO_x removal and NH_3 emissions have been identified and are reviewed. These include mixing, combustion gas temperature, and urea to NO_x mole ratio (NSR).

The data show NO_x removal to increase with the increase in NSR. Over a broad boiler load range (50-100 MW) using an NSR of 1.0, NO_x removal ranged between 43 and 53 percent with NH_3 emissions less than 25 ppm. The use of multiple levels for the injection of urea improves NO_x removal and provides more uniform removal over the load range. It also results in significantly lower NH_3 emissions at reduced loads.

DEMONSTRATION OF AN AUTOMATED UREA INJECTION SYSTEM AT ENCINA UNIT 2

BACKGROUND

The use of urea injection for NO_x emissions control was developed in 1979 by KVB, Inc. (1) under Electric Power Research Institute (EPRI) sponsorship. The process involves the injection of an aqueous urea solution into the boiler furnace to mix with the combustion gas, reducing NO to N_2 and H_2O.

In late 1985, San Diego Gas & Electric (SDG&E) initiated an engineering evaluation of the urea process in Encina Unit 2, a 110 MW gas- and oil-fired boiler. Early tests in 1986 and 1987 focused on characterizing important process parameters and on quantifying the level of NO_x removal that can be achieved (2). Results indicated that urea injection is a viable NO_x control technology for utility boilers and other combustion sources.

Recent efforts, which are the subject of this paper, focused on providing a clearer delineation of the maximum NO_x reduction capability of urea injection and on the development and demonstration of a commercial urea injection system.

OBJECTIVES

The primary objective of this program was to demonstrate that urea injection can be applied commercially to control NO_x emissions during the day-to-day operation of electric utility power plants. Specific objectives consisted of the following:

- Develop an automated commercial urea injection system that can follow changes in boiler load under normal load dispatch conditions and maintain compliance with specific NO_x emission level(s).
- Quantify the NO_x removal capability of the process while maintaining low NH_3 emissions.

- Simplify the design of the urea injectors to improve reliability and ease of maintenance.

- Quantify the composition and concentration of other emissions (CO, amines, etc.) that may result from the use of urea injection.

- Demonstrate commercial system reliability under long term test conditions.

The work addressing the first three objectives has been completed and is discussed in this paper. Work dealing with the remaining objectives will be completed in the first half of 1989.

DESCRIPTION OF TEST BOILER

The demonstration of urea injection was performed on SDG&E Encina Unit 2, a 110 MW gas- and oil-fired boiler built by Babcock and Wilcox (B&W). A side cross-section of the boiler is presented in Figure 1. The boiler is fired with ten burners arranged in two elevations with five burners in each elevation. The unit operates with a balanced draft furnace and is equipped with two vertical-shaft Ljungstrom regenerative air preheaters.

The injection of urea was performed at two elevations. Elevation A (Figure 1) contains nine ports, two on the side walls (ports 1A and 9A) and seven on the front wall. Elevation B contains seven ports, all of which are on the front wall. Urea injection at Elevation A was performed using ports 1A, 3A, 4A, 6A, 7A and 9A. At Elevation B, ports 2B, 3B, 5B and 6B were used. Elevation B is approximately 12 feet below Elevation A.

To avoid making penetrations into the boiler water wall, all ports used for the injection of urea were existing view ports. Depending on the boiler load, the location of these ports did not always correspond to the optimum combustion gas temperature for urea injection.

Testing of urea injection was performed while firing both natural gas and residual fuel oil. Due to current fuel prices and availability, most of the testing was done on oil firing. Baseline NO_x emissions for oil firing as a function of load ranged between 200 and 300 ppm (@ 3% O_2) as presented in Figure 2. All data presented in this paper are for residual fuel oil firing.

AUTOMATED INJECTION SYSTEM

A schematic of the urea injection system is presented in Figure 3. The system was designed to receive 50 percent by weight concentrated urea solution in a storage tank (TK-1). The concentrated urea is batch diluted to 35 percent to prevent crystallization at low temperatures. Urea is transferred from the storage tank (TK-1) to a day tank (TK-2) by a transfer pump (P-1). The operation of the pump is controlled by two level switches located in the day tank (TK-2). The switches transfer urea on demand when the level in the day tank (TK-2) reaches a certain minimum and stops the transfer pump (P-1) when the day tank (TK-2) is full.

The urea is supplied to the boiler by an injection pump (P-2). A water pump (P-3) supplies water to dilute the urea to the final concentration before injection into the boiler furnace. The urea and water are mixed in a static mixer prior to injection.

The flows of urea and water are regulated by two flow control valves. These valves receive their signal from controllers which determine the amount of flow. Two flow meters for the urea and water provide flow indication to the controllers. The injection system can operate with the water flow being directly proportional to the urea flow or can be programmed to maintain a certain total flow.

PROCESS PARAMETERS

Urea process parameters that influence NO_x removal and NH_3 emissions are mixing, combustion gas temperature, urea to NO_x mole ratio and the initial NO_x concentration in the combustion gas. A discussion of each of these parameters is presented below.

Mixing

An obvious requirement for achieving high removal of NO_x is to uniformly mix the urea with the combustion gas. Mixing is affected by the urea injector design, location, and operation and must take into account bulk furnace fluid mechanics which will vary with the boiler design, load and other operating conditions.

The injector design is by far the most important factor in achieving good mixing. Uniform coverage of the furnace cross-section is best provided using wide spray angle injectors and high spray momentum. Atomizers producing coarse sprays at high injection velocity provide the best performance. This is because the large drops with a high injection velocity have sufficient lifetime and momentum to disperse and mix with the combustion gas before the urea is released.

Combustion Gas Temperature

Combustion gas temperature is also an important process variable. It affects both NO_x removal and NH_3 emissions.

Laboratory work sponsored by EPRI (1) has shown a strong dependence of NO_x removal on combustion gas temperature. The maximum NO_x removal was achieved in the laboratory at temperatures in the range of 1800-1900°F. Similar dependence on temperature has been observed in the Encina evaluation. However, high removal of NO_x (>50 percent) was obtained at an average combustion gas temperature ranging from 1460-2000°F.

In a practical application, wide variations in combustion gas temperature exist at any given boiler load. These cause the urea to be exposed to a range of temperatures when injected into the furnace. The NO_x removal achieved thus represents the composite effect of these temperature variations.

Both laboratory and field data have shown NH_3 emissions to be a strong function of combustion gas temperature. Injecting urea at temperatures of 1900°F and higher significantly reduces NH_3 emissions. Injection at lower temperatures (<1800°F) results in a rapid increase in NH_3 emissions. The laboratory data suggested that maximum NO_x removal and low NH_3 emissions could be achieved by injecting urea at the optimum temperature of 1900°F.

Urea to NO_x Mole Ratio

The total amount of urea injected is important. It is expressed in this paper by the term Normalized Stoichiometric Ratio (NSR). This term represents the ratio between the amount of urea injected and the theoretical amount required to reduce all of the NO_x. An NSR greater than 1.0 indicates that excess urea has been injected.

Increasing the NSR provides more urea to react with NO_x. This initially increases the level of NO_x removal achieved. A point of diminishing returns is reached, however, where a further increase in NSR provides only a modest increase in NO_x removal.

The NH_3 emissions dependence on NSR is dominated by the effect of the combustion gas temperature. If the combustion gas temperature is relatively low (<1800°F), a rapid increase in NH_3 emissions results at high NSR. At high combustion gas temperature (>1900°F), the excess urea is oxidized to NO_x, and thus the NSR has only a minimal impact on increasing NH_3 emissions.

Initial NO_x Concentration

The effect of the initial NO_x concentration in the combustion gas on NO_x removal has only been documented in the laboratory. These data show that NO_x removal increases with increases in initial NO_x. The dependence of NO_x removal on initial NO_x has not been observed at Encina. This may be because the change in initial NO_x was not significant (200-300 ppm @ 3% O_2). Other process variables pertaining to combustion gas temperature and mixing in the Encina boiler appeared to influence more directly the level of NO_x removal achieved.

ATOMIZERS SCREENING

The effect of mixing on process performance was evaluated by determining the NO_x removal achieved by different types of urea atomizers. The atomizers examined included several spray patterns with different drop size distributions and were operated at a range of pressures. A description of these atomizers and a discussion of the NO_x removal achieved by each is presented below.

Atomizers Tested

All atomizers tested represented commercially available mechanical atomizers. The spray patterns for these atomizers included three generic types that are labeled for the purpose of this paper as A, B and C. The design details of these atomizers are considered proprietary to the program sponsors.

The atomizers were mounted essentially flush with the furnace walls with minimum penetration into the furnace cavity. This simplified the maintenance and improved the reliability of the injection system.

Atomizer Performance

NO_x removals for the three types of atomizers are compared in Figure 4. The figure presents the range of NO_x removal achieved by each type of atomizer as a function of NSR. The data show that the atomizer design (or urea mixing) can have a significant effect on NO_x removal.

At an NSR of 1.0, NO_x removal ranged from a minimum of 41 percent to a maximum of 48 percent, and at an NSR of 2.0, the removal ranged between 55 and 67 percent. The achieved improvement in process performance by selecting the appropriate atomizer design was 17 percent for an NSR of 1.0 and 24 percent for an NSR of 2.0.

UREA PERFORMANCE - SINGLE LEVEL INJECTION

Laboratory work has shown that combustion gas temperature influences both NO_x removal and NH_3 emissions. To investigate this effect in the field, urea was injected over a range of boiler loads. The urea was injected at either Elevation A or B (Figure 1). For a given boiler load and initial NO_x concentration, this permitted investigation of the effect of combustion gas temperature on process performance.

The change in combustion gas temperature with boiler load was documented on oil firing for Elevation A by performing temperature traverses. A summary of these data is contained in Table 1. The temperature measurements were made at the furnace exit and upstream of the secondary superheater. Ports A2 through A8 were used to make the temperature traverses at the furnace exit, and Ports A1 and A9 were used to make the measurements upstream of the secondary superheater. In general, the average combustion gas temperature is lower at the furnace exit than upstream of the secondary superheater. The data show that the average combustion gas temperature increases from 1460°F to 2000°F as the boiler load is increased from 50 to 110 MW. (Table 1).

No temperature measurements were made at Elevation B. However, based on its position, the combustion gas temperature at this elevation must be higher than at Elevation A because Elevation B is closer to the flame zone. Injecting urea into Elevation B thus provided a qualitative indication of the impact of higher combustion gas temperature on process performance.

Testing was performed using an NSR of 1.0 and 2.0. The number of injectors used at each elevation and their orientation were optimized to obtain maximum NO_x removal. Testing was performed between boiler loads of 50 MW and 100 MW. Full load testing of 110 MW was not possible due to malfunction of a feedwater heater. The dependence of process performance on boiler load (combustion gas temperature) as identified during this testing is presented below.

NO_x Removal

The effect of boiler load (combustion gas temperature) on NO_x removal for an NSR of 1.0 and 2.0 is presented in Figure 5. The figure shows NO_x removal as a function of load using the boiler load as an indirect indication of the combustion gas temperature. The NO_x removals achieved by injecting urea at Elevations A and B are compared.

The data show that NO_x removal is increased with the increase in NSR. At an NSR of 1.0, NO_x removal ranged between 43 and 53 percent; at an NSR of 2.0, the removal ranged between 59 and 68 percent. NO_x removal appeared less sensitive to combustion gas temperature in the field testing. In the laboratory, at an initial NO_x concentration of 500 ppm, NO_x removal dropped from 90 percent to less than 10 percent when the combustion gas temperature was reduced from 1800°F to 1675°F. In the field testing, high removal of NO_x was obtained over a broad boiler load range (50-100 MW). This corresponded to an average combustion gas temperature between 1460°F and 2000°F. For this temperature range, the NO_x removal varied between 59 and 68 percent for an NSR of 2.0. High NO_x removal was thus achieved in the field in spite of the relatively low average combustion gas temperature at which urea was injected.

The moderate dependence of NO_x removal on combustion gas temperatures observed in the field testing is not fully understood. One explanation pertains to the variations in combustion gas temperature that exist at any given load. While an "average" combustion gas temperature may be as low as 1460°F, the variation in temperature can spread over a 350°F range. The NO_x removal observed in the field thus represents the composite effect of a range of temperatures.

Injecting urea at Elevation A provided higher NO_x removals than at Elevation B throughout most of the load range. This trend is the same for the two NSR values tested. The higher removal achieved at Elevation A has been attributed to a more suitable combustion gas temperature for the urea reduction of NO_x.

A peak in NO_x removal has been identified. This shows that the process performance initially improves when the load is increased. Beyond a certain load level (depending on injection elevation and NSR), a deterioration in performance occurs.

The initial improvement in performance with load is explained by the increase in combustion gas temperature. The combustion gas temperature at 50 MW, for example, is lower than optimum (average temperature of 1460°F), and therefore an increase in boiler load (or combustion gas temperature) leads to an improvement in process performance. That is why NO_x removal at 50 MW is higher for Elevation B than Elevation A. Being closer to the flame zone, Elevation B offered a more suitable combustion gas temperature at low load conditions. Increasing boiler load beyond a certain level increases the combustion gas temperature at both elevations. This results in a reduction in the level of NO_x removal achieved.

It must be recognized that many operational variables, including furnace wall cleanliness, furnace excess O_2, burner firing pattern, burner tip cleanliness (in the case of oil firing), and amount of FGR can affect the combustion gas temperature. It is important to be able to quantify the effect of these variables on the combustion gas temperature in order to optimize the urea system performance. Real time combustion gas temperature monitoring during normal day-to-day operation of the boiler would significantly improve the ability to optimize process performance.

NH_3 Emissions

The effect of boiler load (combustion gas temperature) on NH_3 emissions is presented for NSRs of 1.0 and 2.0 in Figure 6. Similar to the NO_x removal data, the combustion gas temperature is represented in the figure by boiler load.

The NH_3 data are consistent with the NO_x removal data and are also in agreement with the data obtained in the laboratory. For both NSR values, NH_3 emissions are lower when urea is injected at Elevation B. A reduction in boiler load or lower combustion gas temperature results in higher NH_3 emissions for both elevations. At very high boiler load (100 MW), the level of NH_3 emissions did not change with the injection elevation (A or B) because the combustion gas temperature is relatively high at both elevations. High NSRs resulted in a corresponding increase in NH_3 emissions, suggesting NH_3 is a byproduct of unreacted urea.

To avoid excessive NH_3, urea should be injected at a relatively higher temperature. According to the laboratory data, the optimum temperature that would provide high NO_x removal and low NH_3 emissions is 1900°F. Again, in a field application, a uniform combustion gas temperature is highly unlikely; therefore, the process performance would reflect the composite effect of existing temperature variations. Injecting urea at the upper end of the temperature range would generally ensure low NH_3 emissions.

UREA PERFORMANCE - BILEVEL INJECTION

Favorable results obtained at each injection level suggested that enhanced process performance would be achieved with multiple injection levels. In a multiple injection configuration, lower NSR is provided at each injection elevation. This improves urea utilization and, in turn, the overall NO_x removal. The lower NSRs also result in reduced NH_3 emissions.

To quantify the potential benefits of this injection method, testing was performed with urea simultaneously injected at both elevations A and B. The split in urea flow to Elevations A and B was optimized for each load to achieve maximum NO_x removal. A computer model based on single level injection data was developed to define the optimum split in urea flow between the two elevations. Urea flow to the top elevation varied from 40-70 percent of the total depending on the boiler load, with the balance of the urea delivered to the bottom elevation. The results of this bilevel injection are discussed below.

NO_x Removal

The effect of bilevel injection on NO_x removal for an NSR of 1.0 and 2.0 is shown in Figure 7. The shaded area in the figure designates the range of NO_x removals achieved by single level injection (injection at Elevation A or B). The plotted data show the removal achieved using bilevel injection.

The bilevel injection results have shown that NO_x removal achieved by this method equals or exceeds NO_x removals obtained with single level injection. More importantly, bilevel injection made NO_x removal essentially constant across the investigated boiler load range. For an NSR of 1.0, the NO_x removal ranged between 43 and 53 percent, and at an NSR of 2.0, the removal ranged between 59 and 68 percent.

NH_3 Emissions

NH_3 emissions with bilevel injection for an NSR of 1.0 and 2.0 are presented in Figure 8. Again, the range for NH_3 emissions obtained with single level injection is shown in the figure by the shaded area. The bilevel injection data are plotted and show a significant reduction in NH_3 emissions at low load. This is the result of reduced NSR at each injection elevation and the injection of a portion of the urea at higher combustion gas temperatures (Elevation B).

PLANNED FUTURE WORK

Additional work is planned in the first half of 1989 to complete the remaining program objectives. The most important part of this work will be performing long term testing of the urea injection system. The purpose of this effort is to verify the system reliability during normal day-to-day operation of the Encina boiler. The intent of the test is to also quantify the long term NO_x emission reduction capability of the technology. Other work to be performed will include the following:

- Assess the NO_x and NH_3 concentration stratification in the Encina boiler flue gas. Use these data to optimize the urea injection rate to improve process performance;
- Determine the urea flow rate required to achieve various specific NO_x emissions target levels. Using these data, program the urea controller to allow operation in the automatic mode while maintaining compliance with specific emission targets;
- Evaluate the automatic operation of the urea injection system when boiler load is changed manually;
- Evaluate the automatic operation of the urea injection system under normal load (dispatch controlled) conditions;
- Quantify the potential for other emissions (CO, amines, etc.).

CONCLUSIONS

Based on the data presented in this paper, the following conclusions are reached:

- Variables that influence the performance of the urea injection process are mixing, combustion gas temperature, and NSR. Based on laboratory data, a combustion gas temperature of 1800-1900°F offers the maximum NO_x removal and minimum NH_3 emissions. Systems should be designed to inject urea as close as possible to this temperature range. Injecting urea at the upper end of this temperature range ensures low NH_3 emissions;

- NO_x removal is increased with an increase in NSR. At an NSR of 1.0, NO_x removal ranged between 43 and 53 percent, with NH_3 emissions of less than 25 ppm;

- Use of bilevel injection improves NO_x removal at high and low boiler loads, providing more uniform NO_x removal over the load range. It also results in low NH_3 emissions at low loads;

- Boiler-specific combustion gas velocity and temperature measurements are necessary for optimum urea injection system design. The use of heat transfer modeling to estimate the boiler combustion gas temperature where measurements are limited also enhances the optimum system design;

- The atomizer design influences the mixing of urea with the combustion gas.

- Although not employed in this program, cold flow modeling may be helpful in selecting the location and orientation of urea injectors to ensure good mixing with the combustion gas.

ACKNOWLEDGMENT

This work was in part funded by Southern California Edison Company (SCE), Electric Power Research Institute (EPRI), Los Angeles Department of Water and Power (LADWP), Consolidated Edison Company of New York (ConEd), and Empire State Electric Energy Research Company (ESEERCO).

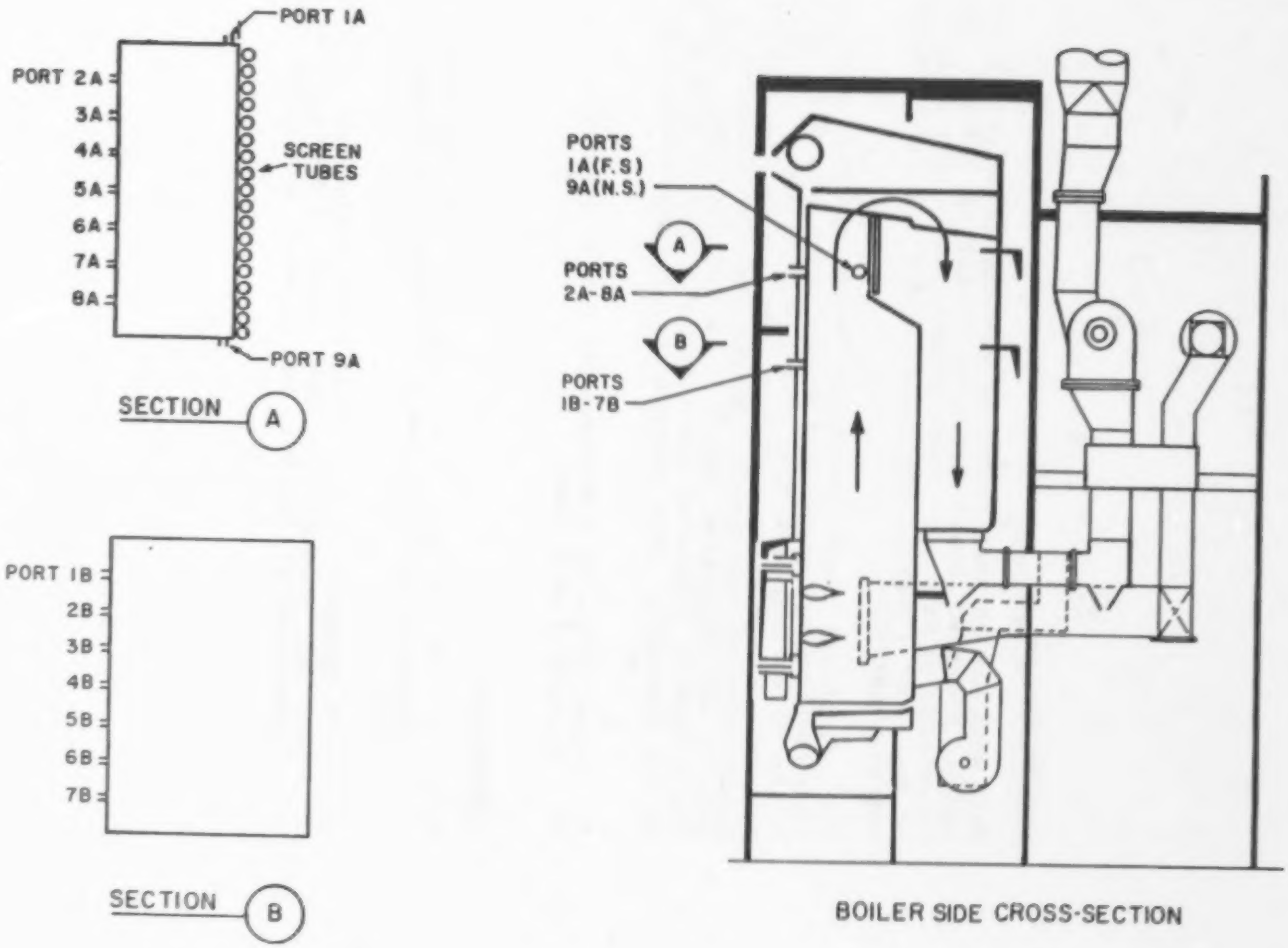
The financial and technical contributions made by these organizations are gratefully acknowledged. Special thanks are due to David Eskinazi of EPRI and Lawrence Muzio of Fossil Energy Research Corporation (FERCO) for their assistance in the preparation of this paper. Thanks are also extended to Robert L. Cravens and Andris R. Abele (1) of AUS for their support of the field tests. Technical contributions made by Greg C. Quartucy (2) of KVB throughout this program are also gratefully acknowledged.

(1) Presently with Environmental Energy Research.
(2) Presently with FERCO.

REFERENCES

1. L.J. Muzio and J.K. Arand. "Homogeneous Gas Phase Decomposition of Oxides of Nitrogen." EPRI Report No. FP-253-1976.

2. M.N. Mansour, et al. "Full Scale Evaluation of Urea Injection for NO_x Removal." 1987 Joint Symposium on Stationary Combustion NO_x Control, New Orleans, Louisiana, March 1987.



SECTION (A)

SECTION (B)

BOILER SIDE CROSS-SECTION

FIGURE 1. SCEMATIC OF ENCINA UNIT 2

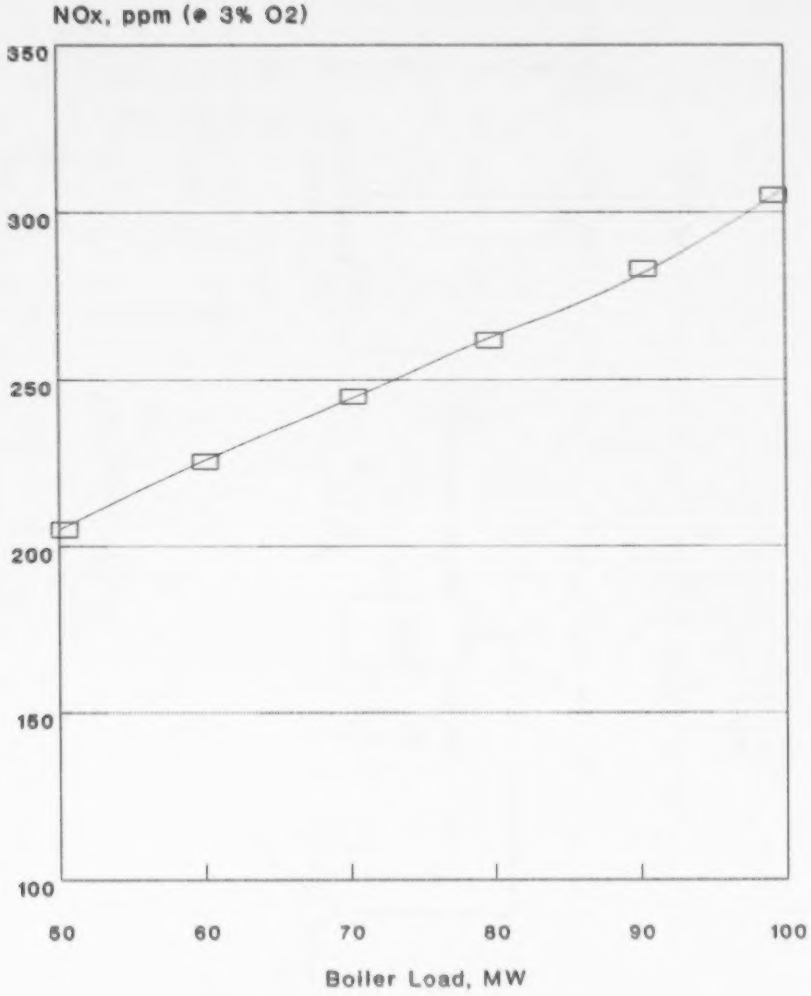


Figure 2. Baseline NOx Emissions – Oil Firing

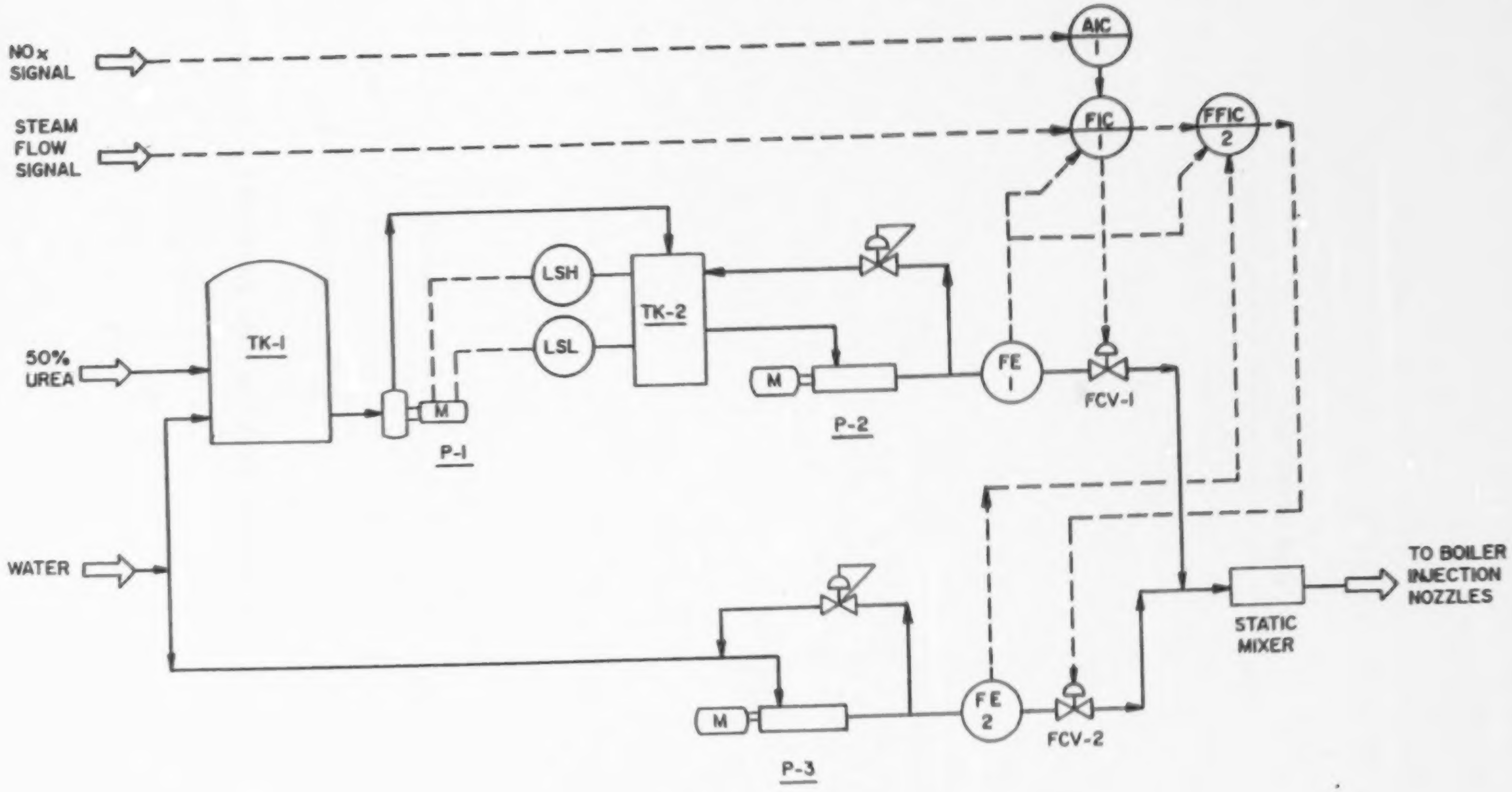


FIGURE 3 UREA INJECTION SYSTEM

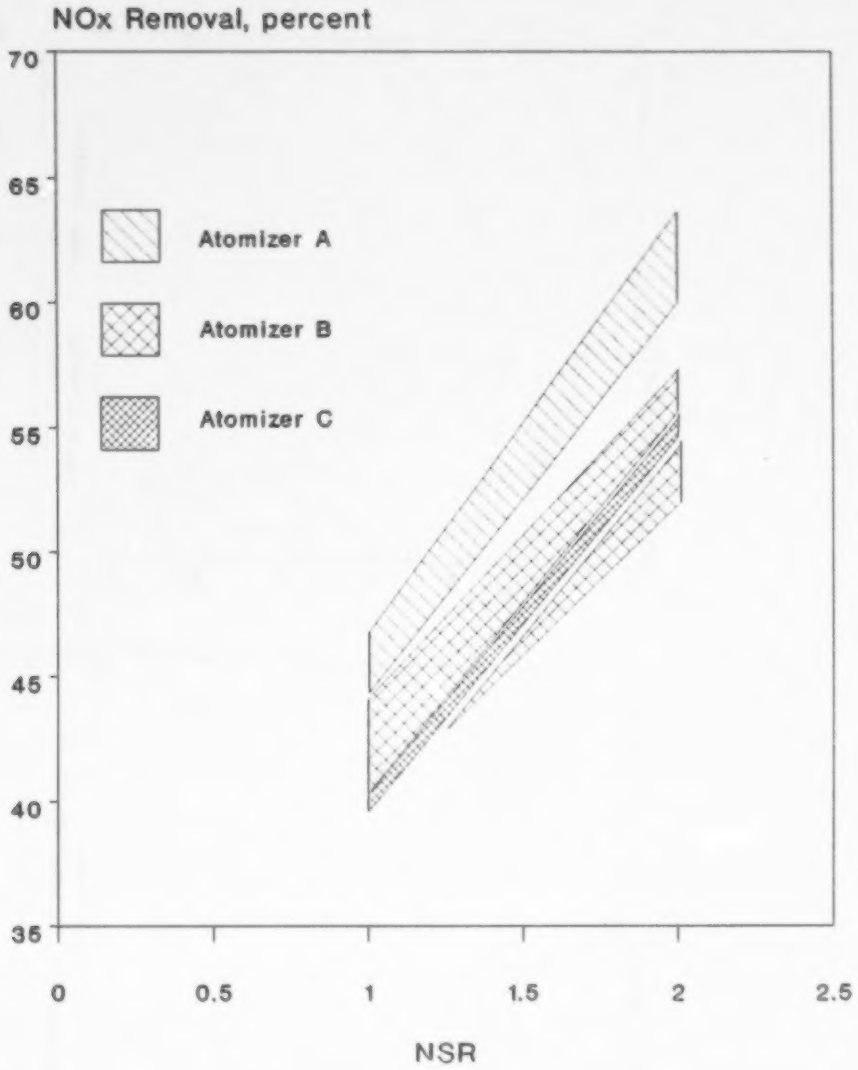


Figure 4. Effect of Urea Atomizer Design on NOx Removal

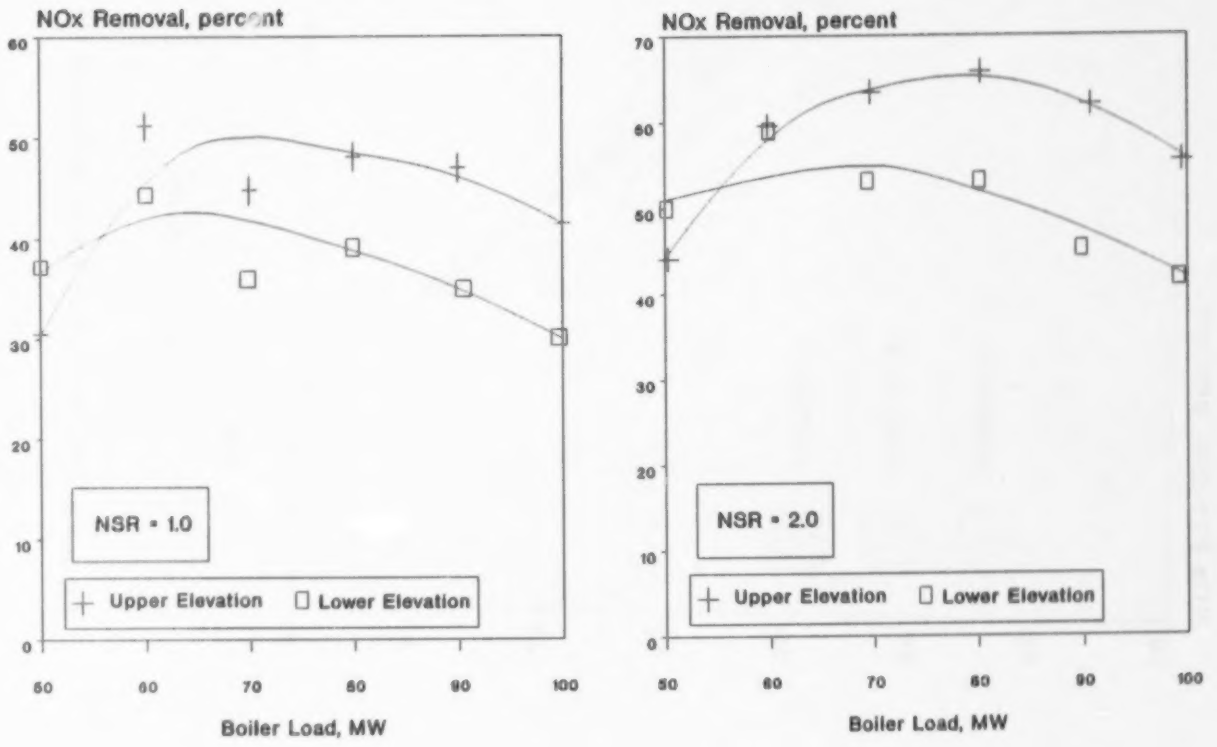


Figure 5. Effect of Combustion Gas Temperature on NOx Removal

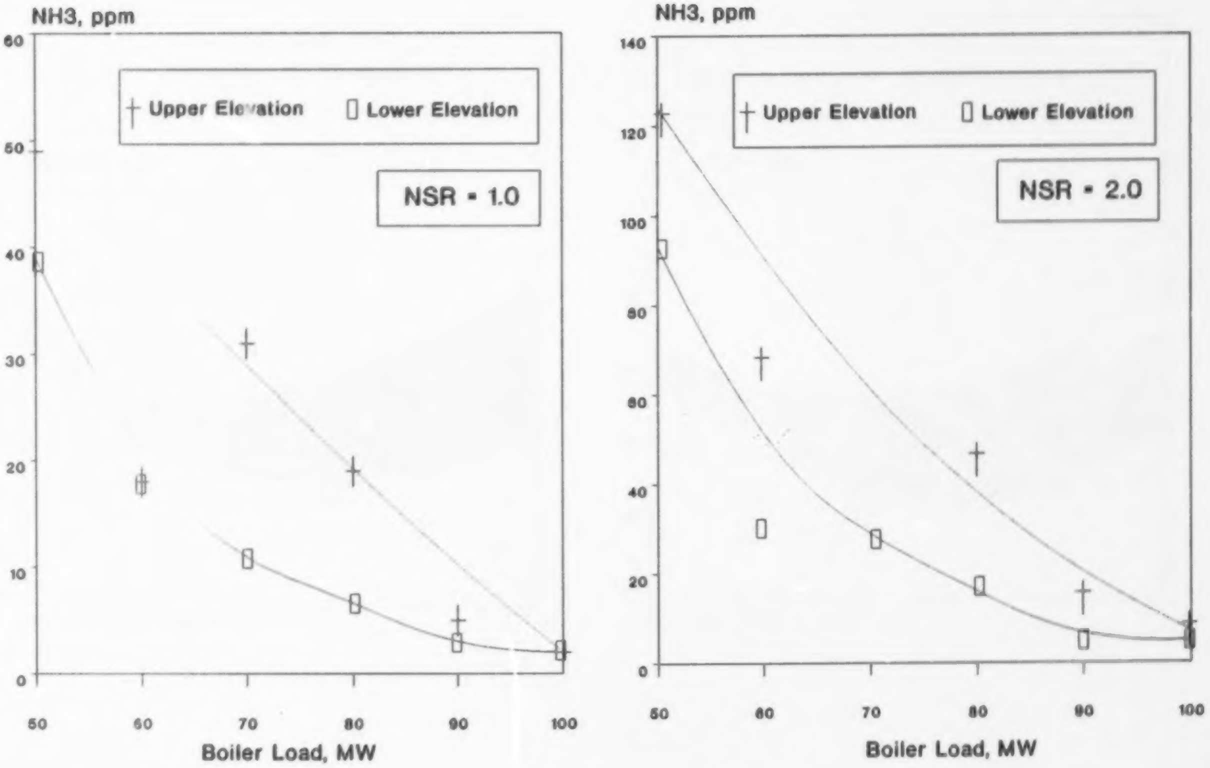


Figure 6. Effect of Combustion Gas Temperature on NH3 Emissions

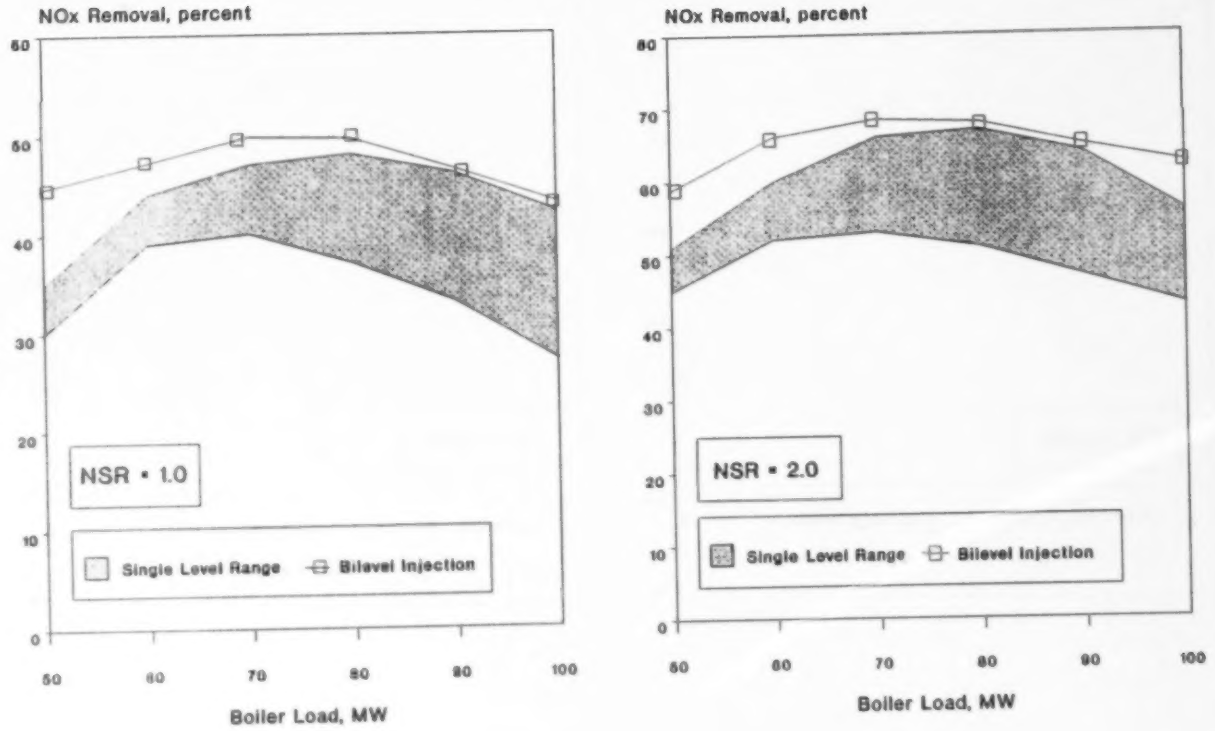


Figure 7. Effect of Bilevel Injection on NOx Removal

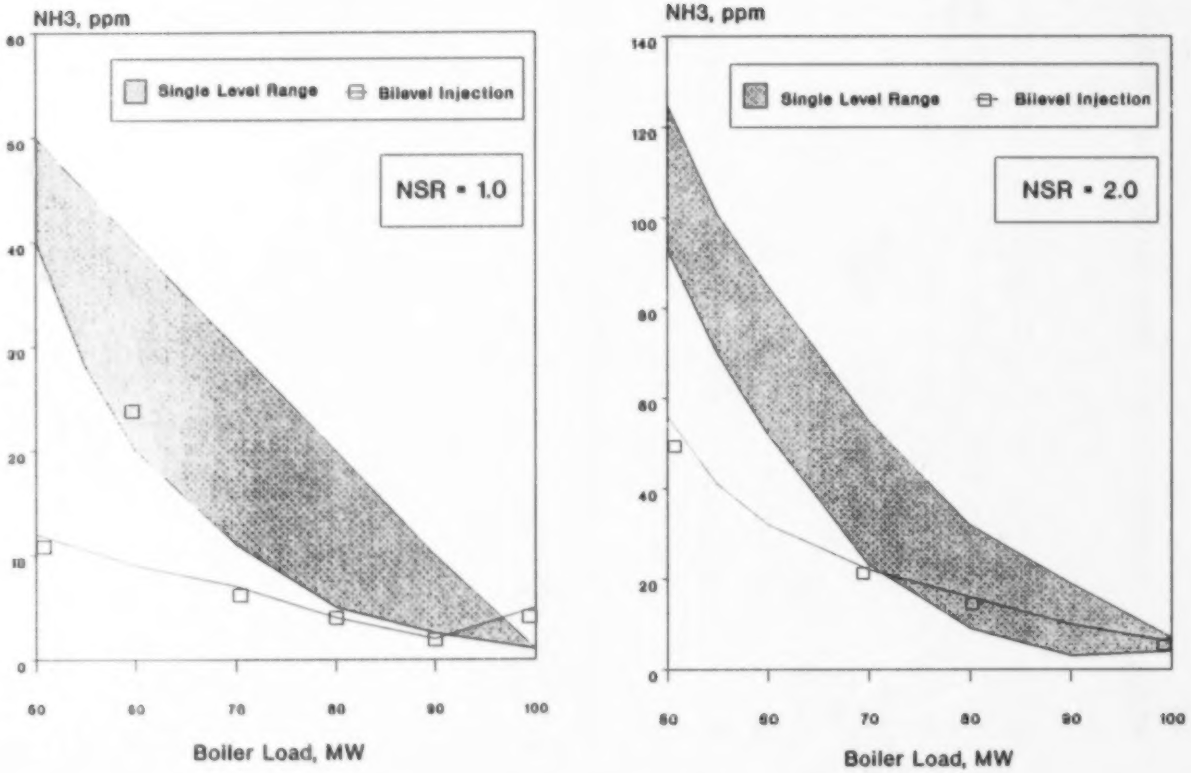


Figure 8. Effect of Bilevel Injection on NH3 Emissions

TABLE 1. COMBUSTION GAS TEMPERATURE DATA SUMMARY - OIL FIRING

	Furnace Exit[1]			Upstream Secondary Superheater[2]		
Boiler Load, MW	Temp., °F	Avg. Temp., °F	Temp. Range, °F	Temp., °F	Avg. Temp., °F	Temp. Range, °F
52	1270-1620	1462	350	1575-1680	1643	105
81	1430-1920	1710	490	1775-1930	1853	155
110	1580-2050	1881	470	1935-2080	2020	145

[1] Ports 2A-8A
[2] Ports 1A & 9A

RETROFIT IMPLICATIONS OF A LOW NOX BURNER SYSTEM ON A 230-MW OIL- AND GAS-FIRED BOILER

James J. Carnevale
Jeffrey A. Klueger
Los Angeles Department of Water and Power
Los Angeles, California 90051

ABSTRACT

The Low NOx Burners were selected as the most appropriate and cost-effective technology to demonstrate a 50-percent NOx reduction on our Haynes Generating Station (HnGS), Unit 3, a Babcock and Wilcox (B&W) 230-MW opposed-fired, oil and gas unit.

The burners are based on Babcock-Hitachi Technology and were purchased from B&W for $1,700,000 on a furnish only basis. The options for additional hardware and engineering support by B&W brought the total contract to almost $2,300,000.

In addition to the burners, the Department anticipates over $9,000,000 in retrofit costs including asbestos removal and disposal; compartmenting the windbox; adding a primary gas injection system; purchasing and installing new flue gas recirculation fans and motors; adding ductwork to mix flue gas into the combustion air; adding ductwork to supply air to the NOx ports; adding new controls; and solving numerous interference and access problems.

This paper will discuss some of the specifics of the retrofit.

BACKGROUND

About four years ago, the Los Angeles Department of Water and Power initiated a study to determine the current state of the art of the various NOx control technologies. One of the objectives of the study was to determine the most cost-effective technology that could be retrofitted to our larger oil- and gas-fired boilers to achieve at least a 50-percent NOx reduction. A second objective was to select one of our boilers to serve as the demonstration unit for a full-scale installation of the selected technology.

The technology selected was the Low NOx Burners, and the demonstration unit selected was our HnGS, Unit 3. The engineering go-ahead for the project was received on January 20, 1987, and testing is scheduled to begin on May 30, 1990 (See schedule Figure 8).

The HnGS, Unit 3, boiler is a 230-MW (B&W), subcritical, single reheat unit that was put into service in August 1964. The details of the boiler design are shown in Table 1.

The HnGS, Unit 3, is currently limited to 125 ppm of NOx while burning natural gas and 225 ppm of NOx while burning fuel oil (both limits at three-percent excess oxygen). These limits are being met by a combination of combustion modifications including four of the 12 burners out of service and overfire air ports (or NOx ports). Gas recirculation is supplied to the hopper only for steam temperature control and is not used for NOx control.

DISCUSSION

The Low NOx Burners are guaranteed to reduce NOx to 65 ppm on gas and 110 ppm on fuel oil containing 0.15-percent fuel nitrogen (both values at three-percent excess oxygen). In order to achieve these guarantees, the following major modifications to the generating unit will be made:

1. Replace the 12 burners with Low NOx Burners of the primary gas-dual register design.
2. Replace the open windbox with a fully compartmented windbox (including asbestos removal).
3. Replace the four overfire air ports with dual register overfire air ports.
4. Add ductwork to direct the flue gas from the discharge of the gas recirculation fan to the mixing plenum where the flue gas is injected through the airfoils into the combustion air.
5. Add a primary gas ductwork system to direct the flue gas to each burner.
6. Replace the two 800-HP (each) gas recirculation fans and motors with two 1,500-HP (each) fans and motors.
7. Replace, modify, and supplement most combustion-related controls and instrumentation .

8. Make numerous modifications to walkways, stairs, and piping systems.
9. Add crossover ducts to both the forced draft and gas recirculation systems to allow unit operation with a forced draft or gas recirculation fan out of service.

In order to better visualize some of the changes required, "Before" and "After" figures are included. Figure 1 shows a cutaway view of the boiler in the current or "Before" condition. Figure 2 is the companion flow schematic for Figure 1. Figure 3 ("After") shows the additional ductwork required to compartment the windbox, to provide preheated air to the overfire air ports, and to provide discrete flue gas to each burner. Figure 4 is the companion flow schematic to Figure 3.

Each of the major modifications listed above is discussed below:

BURNER REPLACEMENT

The originally supplied Peabody burners will be replaced with B&W Primary Gas-Dual Register Burners (PG-DRB). The PG-DRBs (Low NOx Burners) control NOx through the use of delayed mixing, flue gas recirculation, and fuel staging. The Low NOx Burners will allow up to 20 percent of the total flue gas to be recirculated to the combustion process through several different methods.

At some operating conditions, all of the recirculated flue gas (up to 20 percent of the total flue gas) will be mixed through specially modified airfoils into the combustion air downstream of the air preheater. At other operating conditions, the recirculated flue gas flow may be split so that 15 percent is mixed with the combustion air and the remaining five percent will be injected as pure flue gas (primary gas) to the burners. All ignitors and flame detectors will also be replaced.

The existing burners use mechanically atomized fuel-oil guns. Fixed gas spuds are used for natural gas firing. The Low NOx Burners will use steam-atomized fuel-oil guns and adjustable gas spuds for natural gas firing. Provision has been made for the mechanically atomized fuel-oil guns to fit and operate satisfactorily in the Low NOx Burners, and some testing will be done with this configuration. Emissions are not guaranteed for the mechanically atomized guns.

COMPARTMENTED WINDBOX

Although the Low NOx Burners are of the dual register design, the registers are used to control mixing and are not used to control flow. Therefore, in order to properly control and balance flow, each Low NOx Burner requires that an upstream flow-monitoring device and a flow-control device be provided. In order to meet these requirements, our open windbox must be replaced with a compartmented windbox, utilizing 12 separately monitored and controlled flow paths (one to each burner). The additional ductwork required to achieve this is shown in Figure 5. A major cost and schedule impact of this task is the asbestos removal and disposal from the existing ductwork and piping.

OVERFIRE AIR PORTS

The unit is currently equipped with four unsophisticated overfire air ports which will be replaced with four-dual register overfire air ports supplied by B&W as part of the burner contract. One damper and flowmeter upstream of each port will control the total flow to each port. The penetration and mixing of the airflow will be controlled by a sliding damper and spin vanes within each port.

Since the overfire air ports require pure heated air (without recirculated flue gas), their air supply originates just downstream of the air preheater and upstream of the flue gas mixing airfoils. The additional ductwork required to achieve this is shown in Figure 6.

FLUE GAS RECIRCULATION DUCTWORK

This ductwork is new and directs the flue gas from each of the gas recirculation fan discharges to the mixing plenum sections of the combustion air duct. The flue gas is injected through specially designed slots in the airfoils into the combustion air. The air/flue gas mixture is then ducted to each burner. The additional ductwork required to achieve this is shown in Figure 7.

PRIMARY GAS DUCTWORK

This ductwork directs the pure flue gas directly to each burner and is a combination of the existing ductwork (no longer in use) and the new ductwork. This system is shown in Figure 8 with the new ductwork having a circular cross section.

GAS RECIRCULATION FANS

The existing gas recirculation fans provide gas recirculation to the hopper for steam temperature control only. In order to provide gas recirculation to the combustion air and primary gas to the burners, the fan discharge pressure had to be increased. This required new fans and motors with nearly double the existing horsepower (800 each to 1500 each).

INSTRUMENTS AND CONTROLS

Because of the higher degree of control accuracy and speed, as well as the numerous additional monitoring and control inputs required by the Low NOx Burners, a distributed control system was selected to replace the existing pneumatic system. In addition, the added flexibility of a distributed system should simplify start-up.

MODIFICATIONS TO WALKWAYS, STAIRS AND PIPING SYSTEMS

Because of the massive amount of new ductwork required, numerous interferences were created to walkways, stairs, and piping systems. A partial list of interferences is shown in Table 2.

CROSSOVER DUCTS - FORCED DRAFT AND GAS RECIRCULATION FANS

With the existing opem windbox, each forced draft fan is able to feed all 12 burners. With a compartmented windbox, the "A" fan feeds six burners, and the "B" fan feeds the other six with no interconnection from side to side.

In order to ensure stable boiler operation while one forced draft fan is out of service, a crossover duct will be provided to connect the discharge of the two forced draft fans. By the same reasoning, a crossover is required to connect the discharge of the two gas recirculation fans.

ESTIMATED COSTS

Table 3 shows a breakdown of the estimated costs to complete this project.

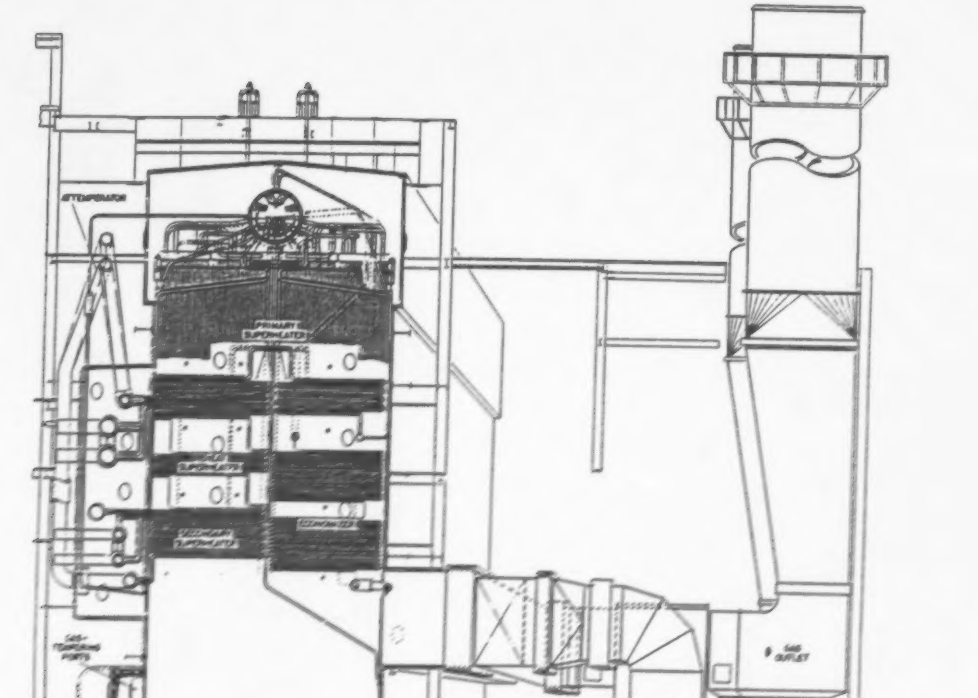


Figure 1

"Before" condition

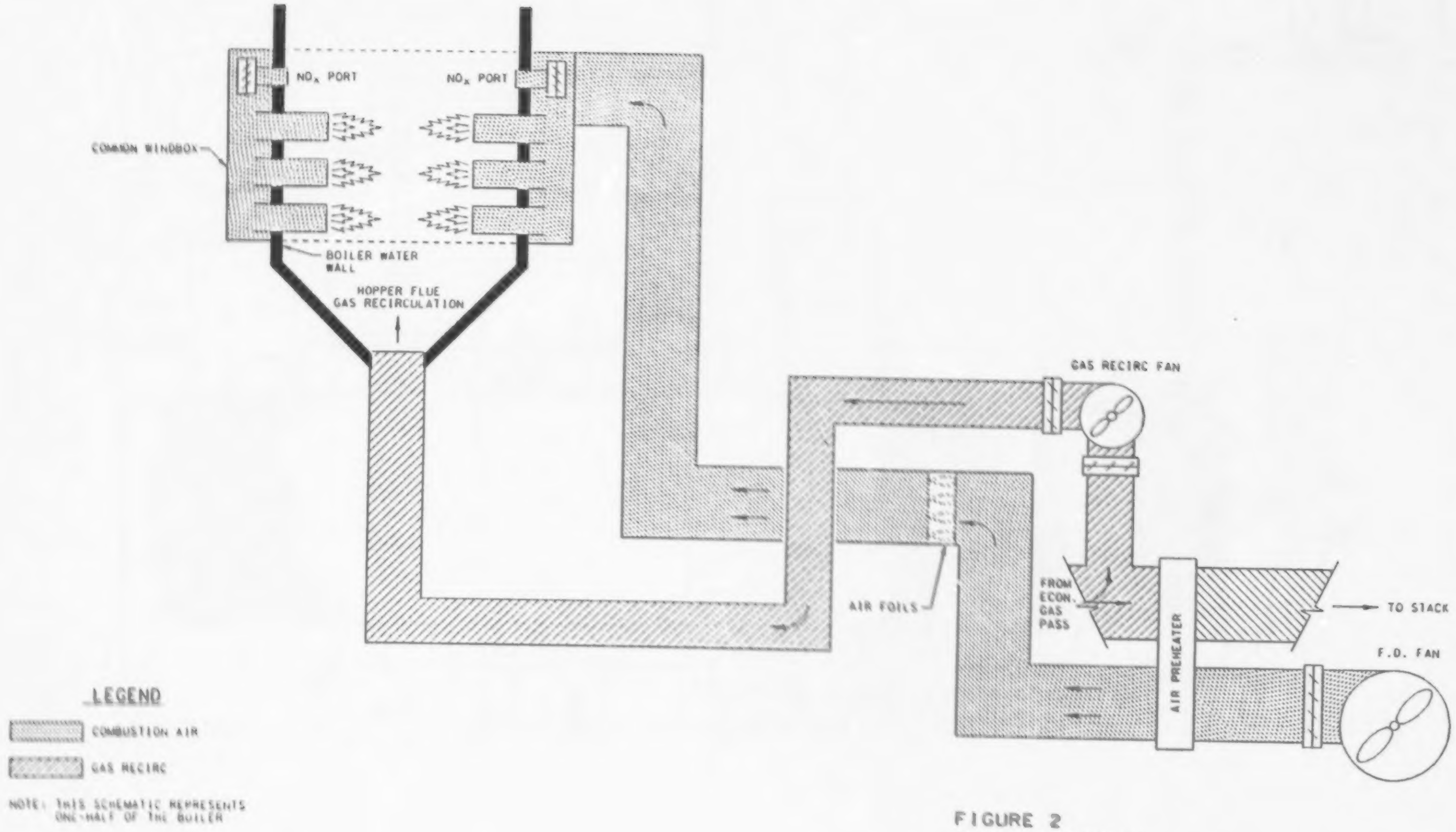


FIGURE 2
FLOW SCHEMATIC
COMBUSTION AIR & FLUE GAS DUCTS
HAYNES GENERATING STATION UNIT 3

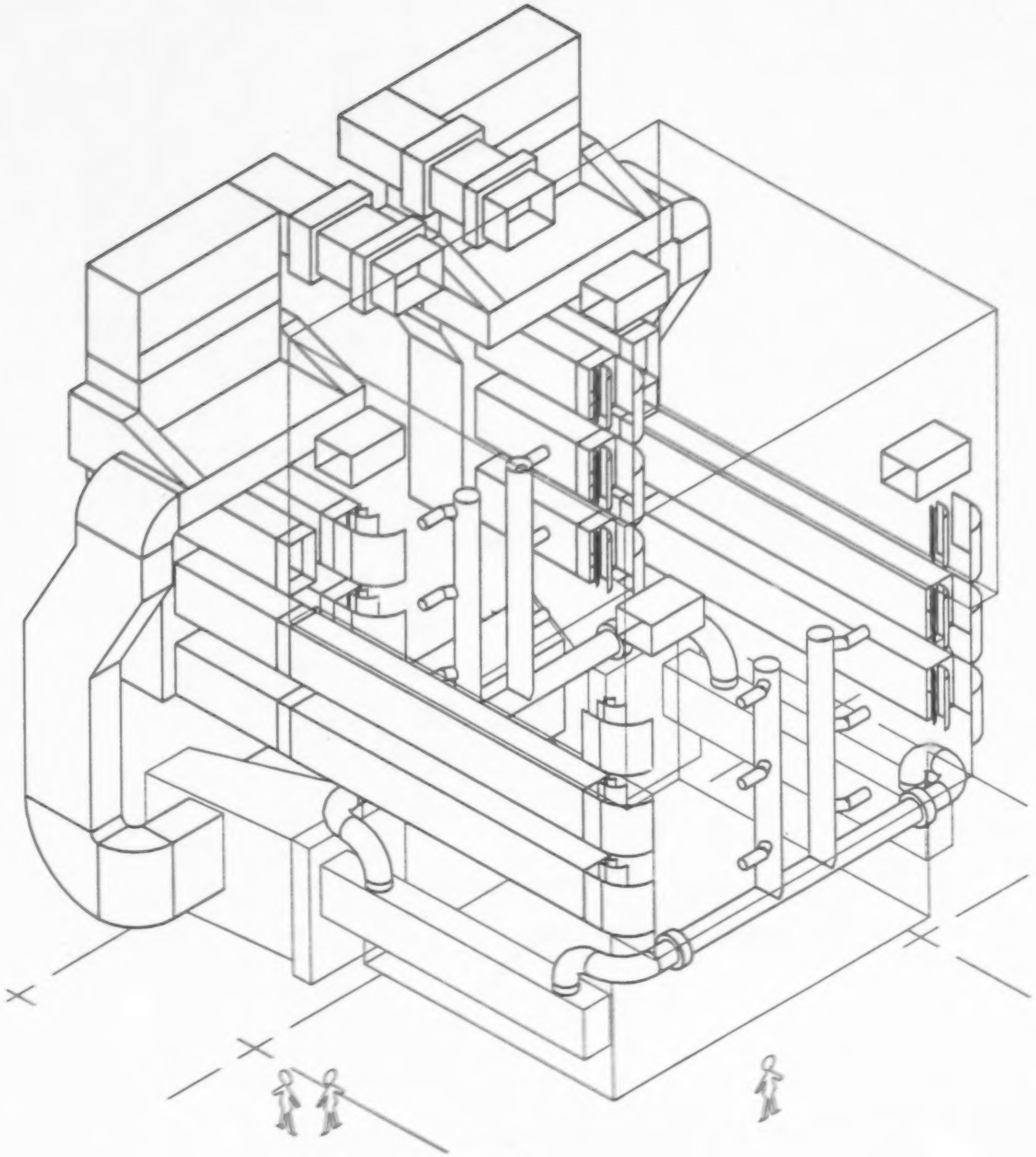


FIGURE 3
LOW NO_X BURNER DUCTWORK MODIFICATIONS
UNIT 3
HAYNES GENERATING STATION

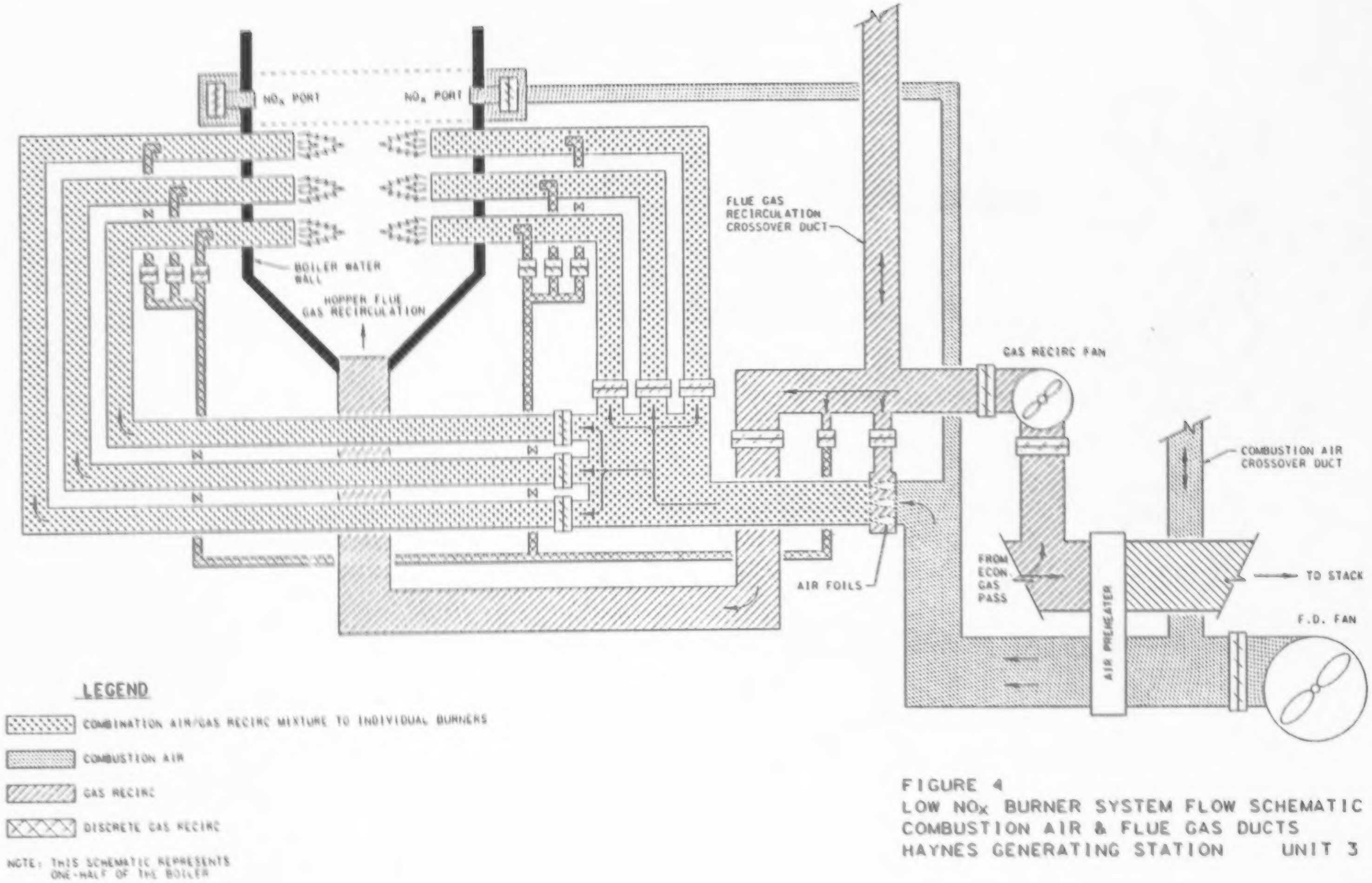

NOx PORT
NOx PORT
BOILER WATER WALL
HOPPER FLUE GAS RECIRCULATION
FLUE GAS RECIRCULATION CROSSOVER DUCT
GAS RECIRC FAN
COMBUSTION AIR CROSSOVER DUCT
FROM ECON. GAS PASS
TO STACK
AIR PREHEATER
F.D. FAN
AIR FOILS
LEGEND
COMBINATION AIR/GAS RECIRC MIXTURE TO INDIVIDUAL BURNERS
COMBUSTION AIR
GAS RECIRC
DISCRETE GAS RECIRC
NOTE: THIS SCHEMATIC REPRESENTS ONE-HALF OF THE BOILER

FIGURE 4
LOW NO_x BURNER SYSTEM FLOW SCHEMATIC
COMBUSTION AIR & FLUE GAS DUCTS
HAYNES GENERATING STATION UNIT 3

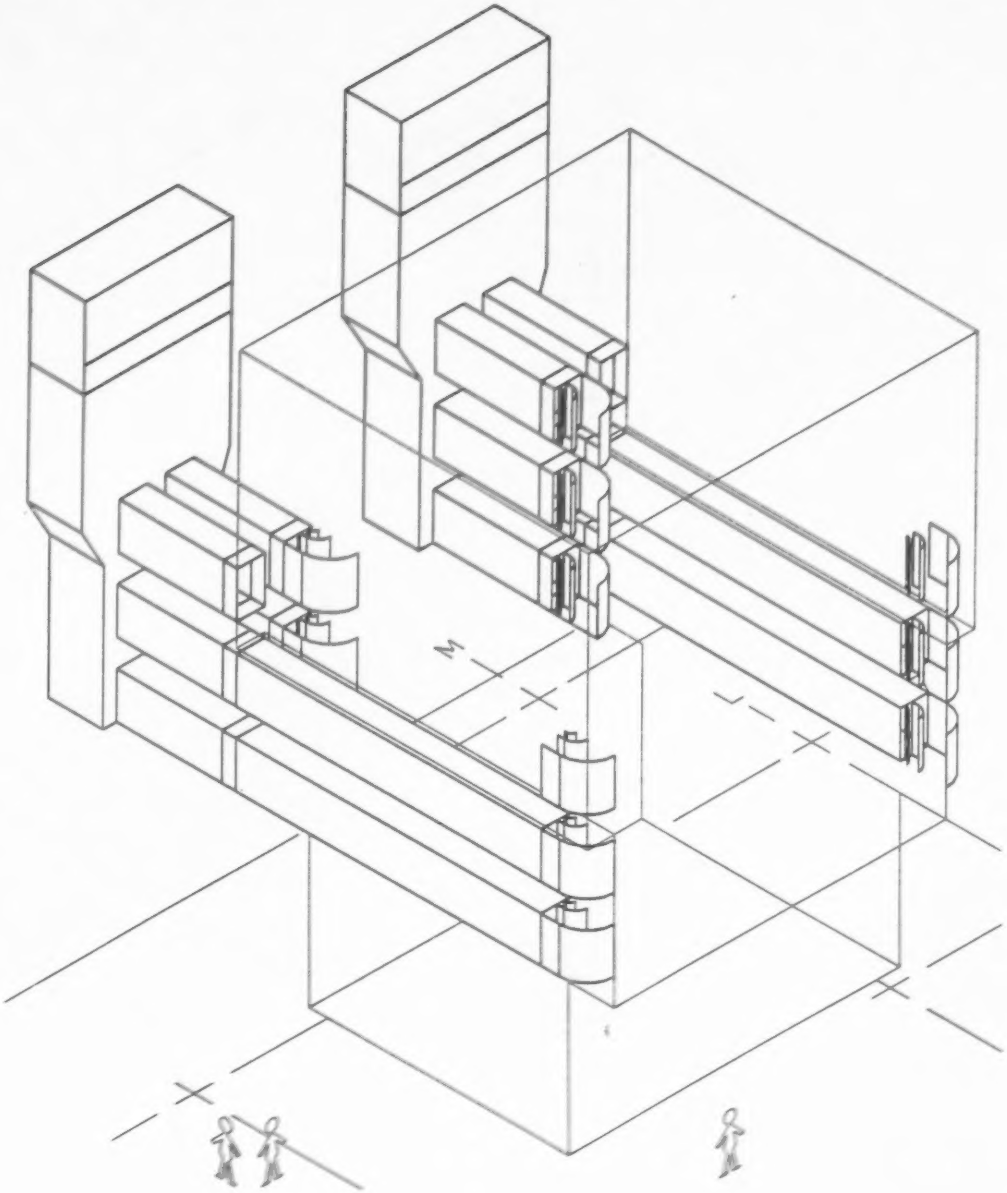


FIGURE 5
LOW NO_X BURNER DUCTWORK MODIFICATIONS
SECONDARY AIR SYSTEM DUCTWORK UNIT 3
HAYNES GENERATING STATION

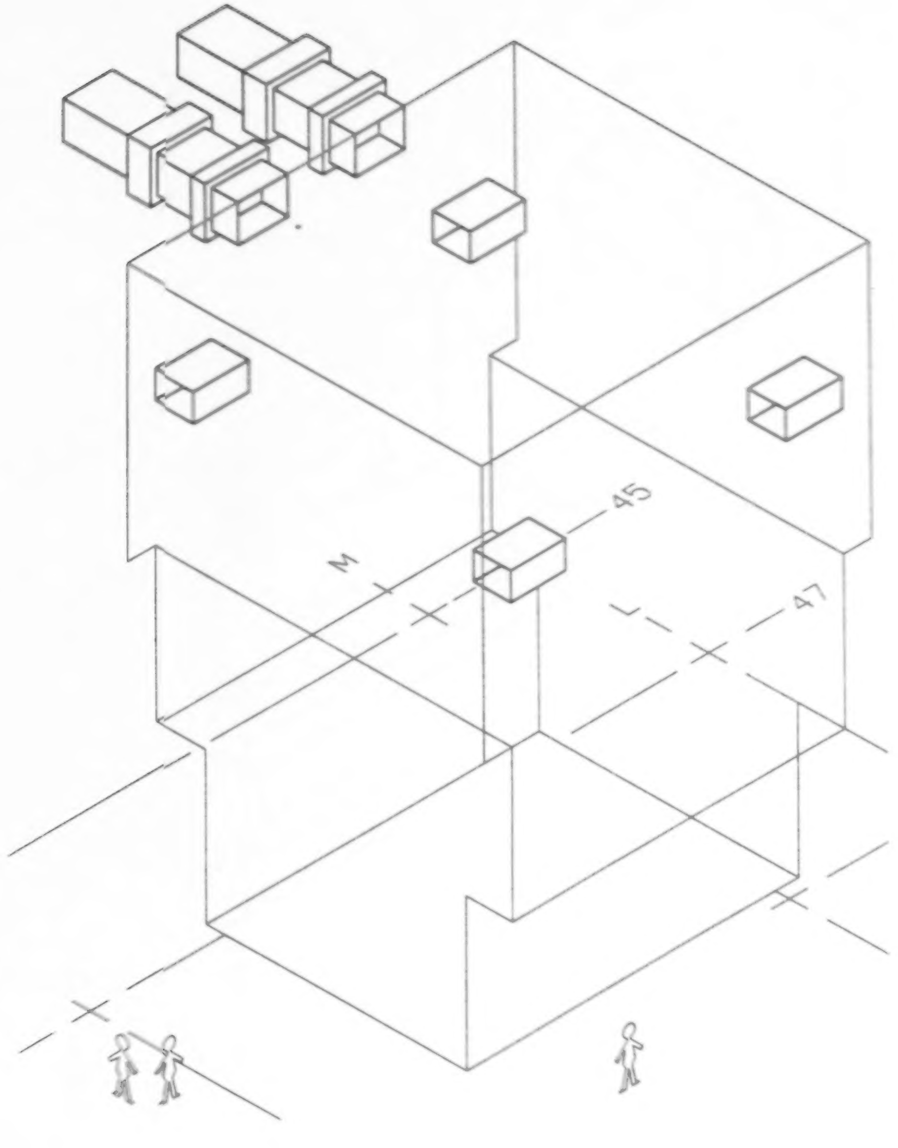


FIGURE 6
LOW NO_X BURNER DUCTWORK MODIFICATIONS
OVERFIRE AIR SYSTEM DUCTWORK UNIT 3
HAYNES GENERATING STATION

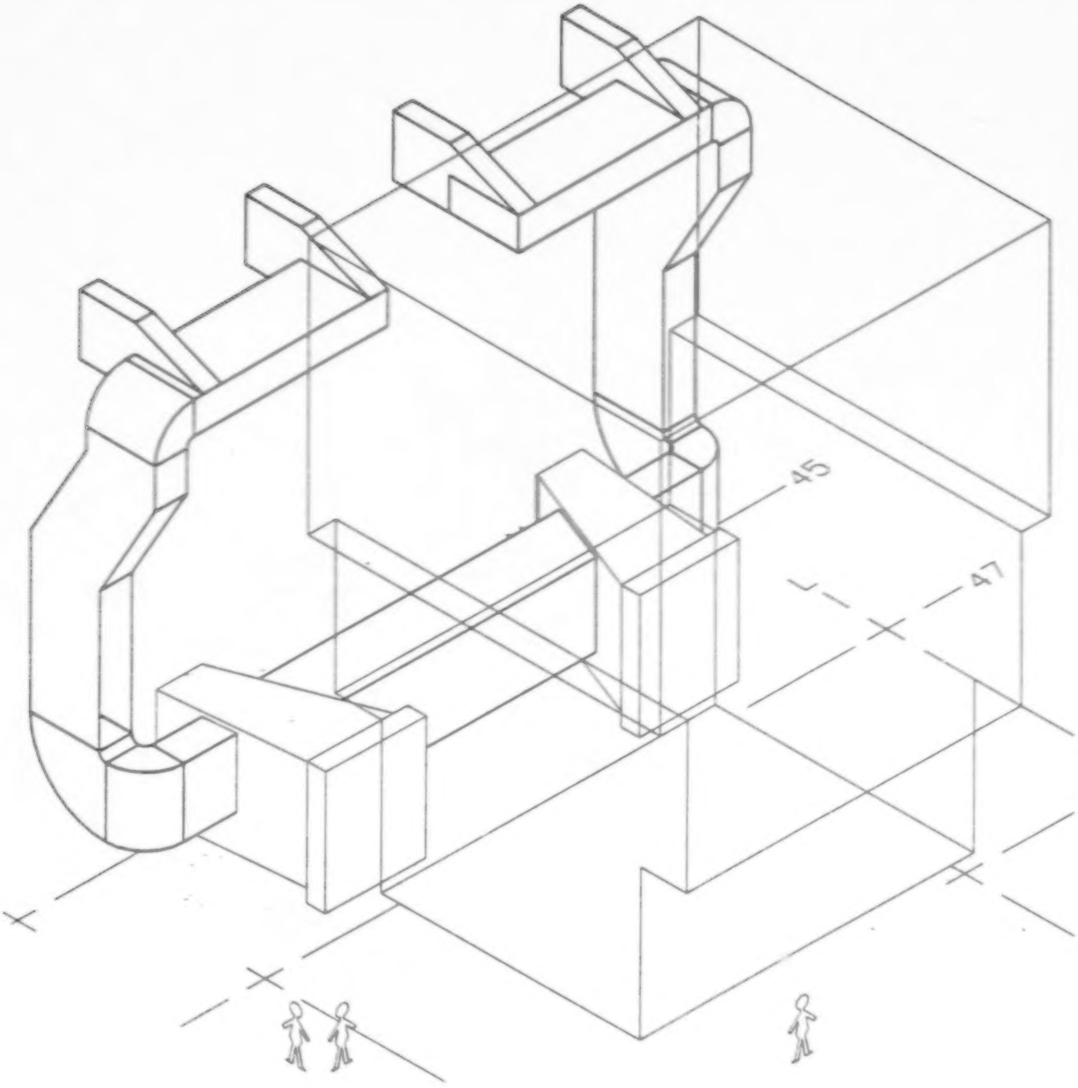


FIGURE 7
LOW NO_X BURNER DUCTWORK MODIFICATIONS
GAS RECIRC SYSTEM UNIT 3
HAYNES GENERATING STATION

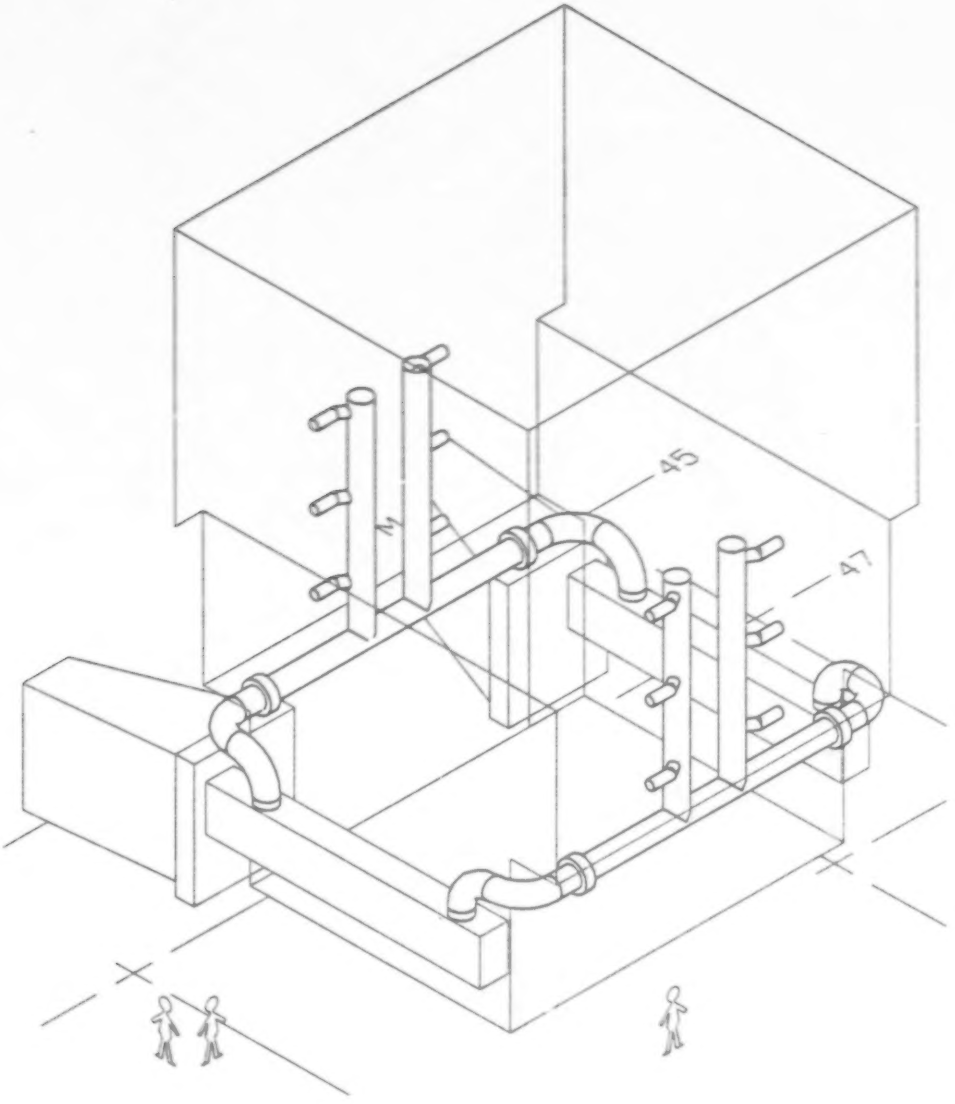
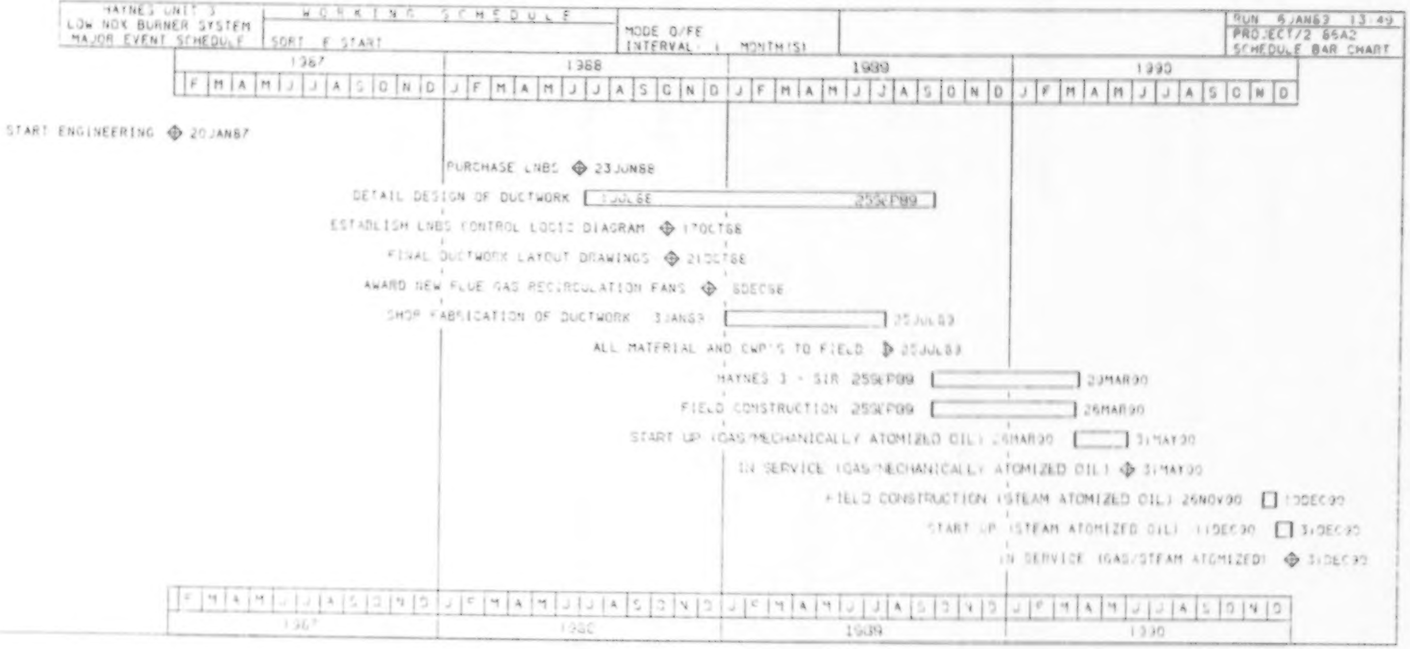


FIGURE 8
LOW NO$_X$ BURNER DUCTWORK MODIFICATIONS
DISCRETE FLUE GAS SYSTEM UNIT 3
HAYNES GENERATING STATION



Reproduced from best available copy.

Schedule

Table 1

Haynes Generating Station, Unit 3
Boiler Design Data

Manufacturer	Babcock & Wilcox
Superheat Steam Conditions	1,575,000 lb/hr 1000°F 2050 psig
Reheat Steam Conditions	1,400,000 lb/hr 1000°F 552 psig
Burners	12 Peabody Mechanically Atomized
Burner Arrangement	Opposed-Fired, 4 per Deck
Fuel	Low-Sulfur (0.25%) Fuel Oil and/or Natural Gas
Gas Recirculation Fans	2 per unit, 800 HP each

Table 2

Haynes Generating Station, Unit 3
Low NOx Burner System Retrofit Cost Summary
List of Interferences

A. Items interfering with Flue Gas Recirculation System.

1. Fire protection piping.
2. Heat tracing steam trap drain waste tank.
3. Horizontal run of five pipes.
4. Walkway support beam.
5. Air heater wash piping valve station.
6. 12-inch seal air lines running north-south on both sides of unit.

B. Items interfering with the Primary Gas Ductwork.

1. Windbox drain valves and piping at both front and rear.
2. A seal air line above tempering air plenum.

C. Items interfering with the Compartmented Windbox.

1. Fire protection hose reels.
2. Burner cabinets and cabinet platforms.
3. All burner piping and control stations.
4. Seal air piping and booster fans.
5. Air heater wash drain piping and access platforms.
6. Two beams.
7. Attemperator valve stations.
8. Walkways.
9. Observation doors.
10. Stair tower.
11. TV cameras and wall openings.

Table 3

Haynes Generating Station, Unit 3
Low NOx Burner System Retrofit Cost Summary

System	Engineering and Material Cost	Demolition and Erection Cost
1. Low NOx Burners, Overfire Air Ports, Dampers, Ignitors, Flame Detectors, and Engineering Support	$2,300,000	$ 700,000
2. Compartmented Windbox (Includes asbestos removal)	$1,000,000	$2,150,000
3. Overfire Air Ports	Included in 1	Included in 1
4. Gas Recirculation Ductwork	$ 300,000	$ 200,000
5. Primary Gas Ductwork	$ 200,000	$ 50,000
6. Gas Recirculation Fans & Motors	$ 700,000	$ 500,000
7. Instruments and Controls	$1,300,000	$ 900,000
8. Modifications to Stairs, Walkways, and Piping Systems	$ 700,000	$ 500,000
9. Crossover Ducts	$ 150,000	$ 150,000
Subtotals	$6,650,000	$5,150,000
Total	$11,800,000	

RETROFITTING LOW-NO_X BURNERS FOR GAS AND OIL FIRING

J. Gerdes, Jr. & R. Waibel
John Zink Company
Tulsa, Oklahoma, USA

L. Radak
Southern California Edison Co.
Rosemead, California, USA

ABSTRACT

There is a growing necessity to consider environmental concerns in the operation of all commercial combustion processes. Controls on emissions released to the environment are being tightened across the nation and indeed throughout the world. However, performance aspects are as important as emissions, especially to the operators of the facilities. It is important to understand both the capabilities of new emission control technology and how that technology will affect system reliability and operating flexibility, especially when retrofitting to existing equipment.

The John Zink Company has been engaged in a continuing program with the Southern California Edison Company to apply Zink's low NO_X staged fuel technology to utility boiler burners. Development and testing has been conducted on various sized units ranging from 25 million Btu/hr to 122 million Btu/hr. Ambient air, preheated air and flue gas recirculation tests have been conducted. The latest John Zink boiler burner development work involves full scale testing of both a 95 million Btu/hr staged fuel AVC burner designed to operate with flue gas recirculation and a 122 million Btu/hr staged fuel/staged air AVC burner. Special attention has been paid to burner operating characteristics that affect stability and reliability.

INTRODUCTION

There is a growing emphasis on controlling all types of emissions emanating from industrial and commercial processes, not the least of which is combustion related emissions. Due to recent and pending legislation, most utilities are faced with the need to reduce NO_x emissions. The Southern California South Coast Air Quality Management District has been a leader in the effort to control the amount of combustion products released to the atmosphere. Available NO_x control options tend to fall into one of two groups - control of the combustion process (and thereby the production of NO_x) or chemical/catalytic treatment of the NO_x laden exhaust stream. The former, control of the combustion process, tends to be a less expensive approach. Southern California Edison (SCE) has been engaged in a program with John Zink Company to develop the burner retrofit technology to economically control the production of NO_x emissions through combustion system design. Although maintaining acceptable emission levels is critical from the environmental aspect, the affect any new NO_x control technology has on reliability and system operation is equally important and should be understood.

COMBUSTION SYSTEM NO_x CONTROL METHODS

There are several methods of controlling NO_x formation through burner design and combustion system modifications. These include: burners out of service; low excess-air operation; flue gas recirculation; air staging; and fuel staging. These techniques reduce NO_x emissions either by controlling the peak flame temperatures or by limiting oxygen availability in the region of peak flame temperature. Before the discussion of this specific work, a brief description of each of these techniques is given below.

FUEL STAGING

Staged fuel NO_x control, developed and patented by John Zink Company, is accomplished by injecting part of the fuel together with all the combustion air into the primary combustion zone. Thermal NO_x production in this region is limited by the low flame temperatures that result when fuel is burned with high excess air levels. NO_x production is low despite the high oxygen concentrations because peak flame temperatures are low. The remainder of the fuel is then injected into the tail of the flame emanating from the primary combustion zone. Partial combustion of the fuel in the primary region provides inerts that reduce peak flame temperatures in the secondary combustion zone while lowering the local concentration of oxygen. Both factors limit the NO_x production in the secondary combustion zone.

Fuel staging is the most effective burner design technique of controlling gas fired thermal NO_x. Flame lengths for staged fuel flames are shorter than comparable staged air flames and, unlike air staging, low excess air levels are possible. Excess air levels of 5% (1% excess O_2) or less are possible, which further enhance emission reductions.

AIR STAGING

For NO_x control with fuels containing fuel bound nitrogen, such as No. 6 oil, the most effective NO_x control technique is air staging. NO_x generated with such fuels comes from two sources - thermal NO_x and fuel NO_x (that attributable to fuel bound nitrogen).

Air staging is accomplished by dividing the combustion air into two or more streams. A sub-stoichiometric volume of the air is introduced in the primary zone to form a fuel rich combustion region in which the fuel is only partially burned. A portion of the fuel bound nitrogen decomposes to form molecular nitrogen thus reducing fuel NO_x formation. The localized sub-stoichiometric operation also lowers the peak flame temperature thereby reducing the thermal NO_x generated.

The rest of the air is injected down stream of this fuel rich primary combustion zone forming a secondary burn-out region in which combustion is completed. NO_x formation in this secondary combustion zone is limited because primary zone products of combustion reduce both the flame temperature and oxygen concentration.

BURNERS OUT-OF-SERVICE/OVER FIRE AIR

Operating with burners out-of-service is a rudimentary form of air staging. This technique utilizes burners fired sub-stoichiometrically with the additional combustion air added elsewhere in the firebox. Some systems provide this supplemental air through "Out-of-Service", upper tier burners, while other systems have dedicated air ports located above the firing burners (ie. "Over Fire Ports) which provide this air.

LOW EXCESS AIR

Low excess air operation provides some control over production of both thermal and fuel NOx by reducing the availability of oxygen during combustion. The level of control attainable, however, is limited because combustion efficiency suffers as excess oxygen levels approach zero. Operation at very low levels of excess oxygen results in increased carbon monoxide and soot emissions.

FLUE GAS RECIRCULATION

Flue gas recirculation (FGR) combined with low excess air operation provides a reduction in thermal NO_x, although it has little effect on NO_x caused by fuel bound nitrogen. The recirculated products of combustion injected into the combustion air stream provide inert gases which lower the adiabatic flame temperature and, to some extent, the local oxygen concentration. Beyond 15% FGR, the incremental effectiveness of added flue gas recirculation diminishes. The maximum FGR level is generally limited by flame stability to about 25% to 30%.

EXPERIMENTAL SETUP

The John Zink Company International Research Center includes nine test furnaces of various sizes and configurations that allow testing of burners ranging from less than 1 million Btu/hr heat release to over 250 million Btu/hr. Burner development work is typically conducted on full scale equipment, in this case burners rated for 95 million Btu/hr and 122 million Btu/hr. Testing full sized equipment under conditions simulating the customer's field operating conditions permits the direct interpretation of the data. It also permits testing of upset or startup conditions in a controlled manner rather than on-line in the field.

The furnace used for this testing (Furnace #3) is a cylindrical, horizontally fired, water jacketed chamber, 11 feet in diameter by 29 feet long. Integral to the furnace design are 15 sight ports providing an unobstructed view of the combustion process. Forced draft combustion air was supplied through adjacent ductwork. The system can be configured for either ambient air or preheated air (500°F - 600°F) operation at rates in excess of 122 million Btu/hr. In addition, the system can be configured to simulate FGR operation (up to 25%) at various burner inlet air temperatures.

The furnace draft and windbox pressures were measured using manometers. A suction pyrometer measured stack gas temperatures. Stack emissions (O_2, CO & NO_x) were continuously monitored using a water cooled probe to obtain exhaust gas samples. The samples were dried and filtered using a Thermo Electron sample conditioning system. NO_x was measured with a Thermo Electron Chemiluminescent Model 10 analyzer; oxygen with a Teledyne Model 326A analyzer; and carbon monoxide with a Thermo Electron Model 48 Gas Filter Correlation CO Meter. All instruments were calibrated before and during testing using certified span gases.

Typically the fuels tested are natural gas and fuel oil, ranging from diesel oil to #6 oil. However, the John Zink test facility has the capability of using customer supplied liquid fuels or blending various gaseous components to simulate specific fuel composition. Gas firing rates are determined using the burner pressure vs. heat release capacity curve after verification of the capacity curve with a turbine meter. Oil flow rates are determined using inline flow meters.

BURNER DESCRIPTION

Figure 2 depicts John Zink's patented staged fuel burner design. It shows a cross-sectional view of an AVC boiler burner. The John Zink AVC (Adjustable Vortex Control) series boiler burner offers maximum flame pattern adjustability with a wide range of flame stability. The AVC design allows operation at excess air levels of less than 0.5% excess oxygen. The AVC burner is available in four basic designs; the standard emission series, the staged air series, the staged fuel series, and the combined staged fuel/staged air series.

The "Adjustable Vortex Control" assembly allows a full range of air control from axial flow to high swirl. The main burner air is divided into two streams designated primary and secondary air, each with their own control register. On "Staged Air" burners, tertiary air registers are added. This permits control of the air going to the secondary combustion zone.

The AVC burner design utilizes different NO_x control mechanisms for oil and gas operation. Tertiary air on fuel oil firing provides the air staging for NO_x control. On natural gas, staged fuel is used to control NO_x emissions. Fuel staging is accomplished on gaseous fuels using primary and secondary fuel injectors.

The results given herein are based on the testing of three burners, including comparisons to previous results reported in "Fuel Staging Burners for NO_x Control." The current work compliments the earlier results with information obtained on larger capacity burners. The burners tested were:

- Staged Fuel AVC rated for 95 million Btu/hr, gas fired with Flue Gas Recirculation with 330°F
- Staged Air/Staged Fuel AVC rated for 122 million Btu/hr, No. 6 fuel oil and gas fired with 620°F preheated air

The data from these tests are compared with data from previous tests on similar AVC burners reported in "Fuel Staging Burners for NO_x Control."

DESCRIPTION OF TESTS AND RESULTS

OIL FIRING

Although the bulk of the development work was concentrated on natural gas firing, limited testing was done with a standard John Zink PM oil atomizer - a six-port, steam assisted Y-Jet type oil gun. The fuel used was a heavy fuel oil with 0.3 wt percent fuel bound nitrogen. CO emissions were low under all conditions. Most readings ranged from 0 ppm to 50 ppm, with the highest being 103 ppm. At the normal heat releases, the NO_X ranged from 234 ppm to 250 ppm.

The oil flames were well defined. At high fire the oil flame tended to be straight and narrow. At a firing rate of 122 million Btu/hr and 3% excess oxygen, the flame envelope was approximately 10 feet in diameter and 26 feet long. As the oxygen was reduced to 2%, combustion intensity decreased and the tip of the flame occasionally reached into the furnace stack.

GAS FIRING

Utility boilers require burners with broad operating envelopes to ensure reliable operation even during upset conditions. Multiple burner units need the capability of lighting both the pilot and main fuel on out-of-service burners while the system is under load. For this reason it was important to determine the stability of an individual burner at low fuel firing rates with the combustion air at maximum flow.

The AVC gas burner was demonstrated to be stable under a variety of system upset conditions. The primary gas injectors and the tile profile have been designed to provide a stable region to burn the primary fuel. This serves a piloting function for fuel injected into the secondary combustion zone. Specific upset conditions that were tested and were demonstrated to be stable included:

- Pilot lightoff with full air flow
- Main burner lightoff at low fire with full air flow
- Full burner air flow with minimum gas flow
- Full burner air flow rapidly spiking fuel flow from low to high fire and back to low fire
- Minimum fuel flow rapidly spiking air flow from low to high fire and back to low fire
- Stable operation with cooling steam flowing through the oil gun

Figure 3 shows stable operation points with full air flow. Fuel turndown with both the primary and secondary fuel injectors in operation is approximately 4:1, limited by the stability of the flame in the secondary combustion zone. As illustrated, turndown can exceed 20:1, even with full air, if the secondary fuel injectors are turned off.

The NO_x emissions for the 122 million Btu/hr AVC staged fuel/staged air burner were compared with previous data on two 100 million Btu/hr AVC burners (one staged fuel burner, one conventionally fired burner). Data from the most recent test correlate well with the previous data. The results presented in Figure 4 show that under the test conditions, fuel staging reduced NO_x emissions by 50% compared to a conventionally fired burner with ambient air and by nearly 70% with 600°F preheated air.

FLUE GAS RECIRCULATION

When very low NO_x levels are required, flue gas recirculation (FGR) can be combined with fuel staging to achieve exceedingly low NO_x emissions. Figure 5 shows the results of two staged fuel AVC burners tests - a 95 million Btu/hr burner operated at 330°F preheated air and a 50 million Btu/hr burner operated at 500°F preheated air. The data presented in Figure 5 indicate the effect on NO_x emissions with varying percentage of flue gas recirculation on staged fuel burners. Greater than a 50% reduction was observed as the percentage of flue gas recirculation was increased from 0% to 25% on both stage fuel burners. Note that the data show that a burner operating with 500°F preheated air in a 2200°F combustion chamber provides NO_x emissions similar to a burner operating with 330°F preheated air in a 2400°F combustion chamber. It is well known that NO_x is strongly influenced by factors that affect the peak flame temperatures. Some of the most important factors that influence flame temperature, in addition to fuel composition, are air preheat temperature and combustion chamber operating temperature.

CONCLUSIONS

There are two equally important aspects of utilizing low NO_x technology to control process emissions. The first is the level of emissions obtained with this technology. The second is the affect on operations of implementing this technology. John Zink Company has developed information in both areas using full scale equipment. Test results have been presented indicating a reduction in NO_x on the order of 50% or more with staged fuel over a conventionally fired burner, depending on operating conditions. A further reduction of 50% is obtained when FGR is used in conjunction with fuel staging.

The data from these recent tests show that it is possible to design a low NO_x burner that can also meet stringent stability requirements. In addition, the recent data correlate well with the previous data. The data confirm the dependence of NO_x generation on combustion chamber and air preheat temperature. The data also confirm the ability of fuel staging combined with FGR to produce very low NO_x levels.

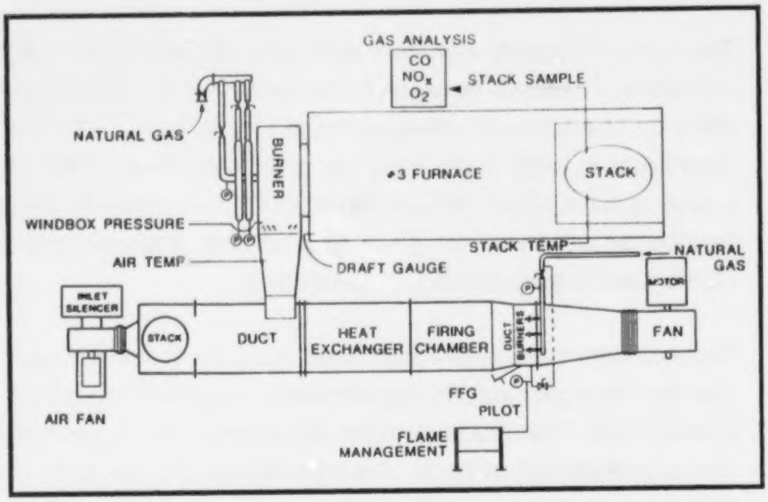


Figure 1. Staged Fuel Boiler Burner Test Installation

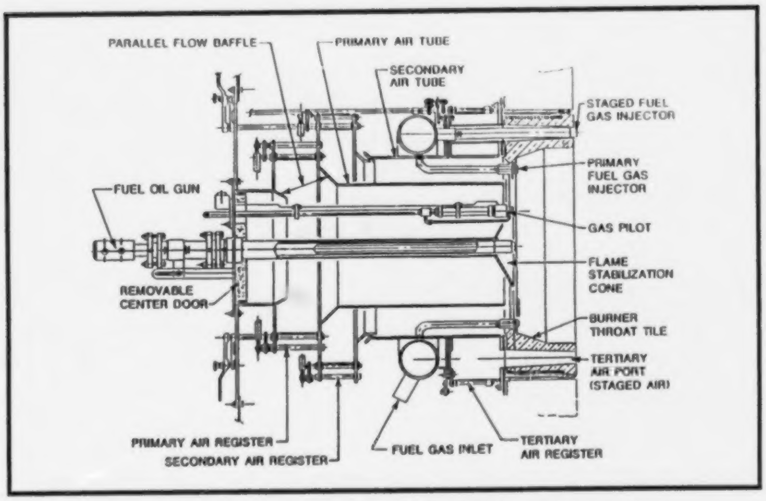


Figure 2. John Zink Staged Fuel/Staged Air $LoNO_x$ AVC Boiler Burner

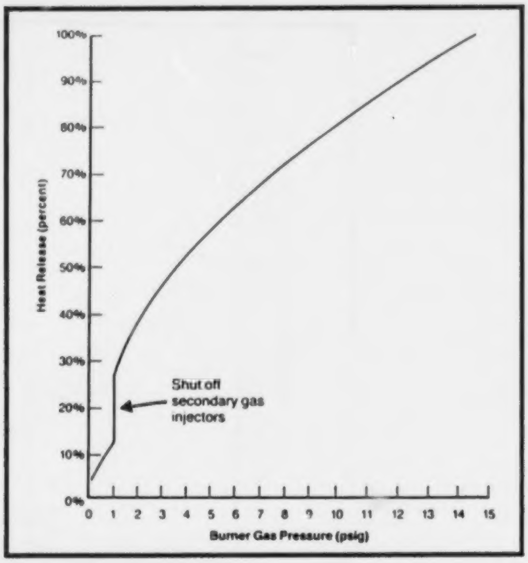


Figure 3: Extended Burner Turndown with Maximum Air Flow

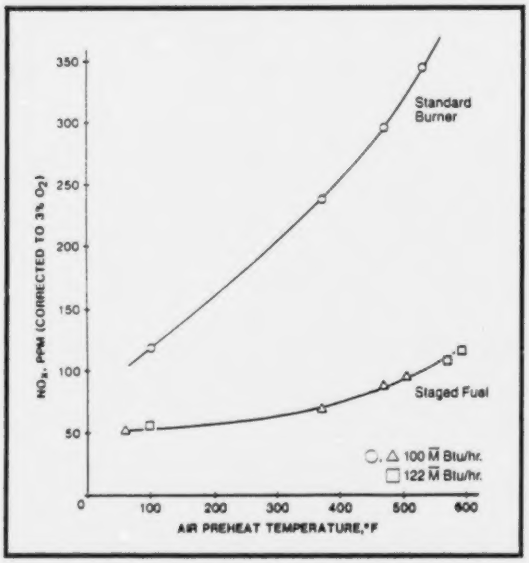


Figure 4. Comparison of NO_x vs. Air Preheat for Various Firing Configurations at 2% Excess Oxygen

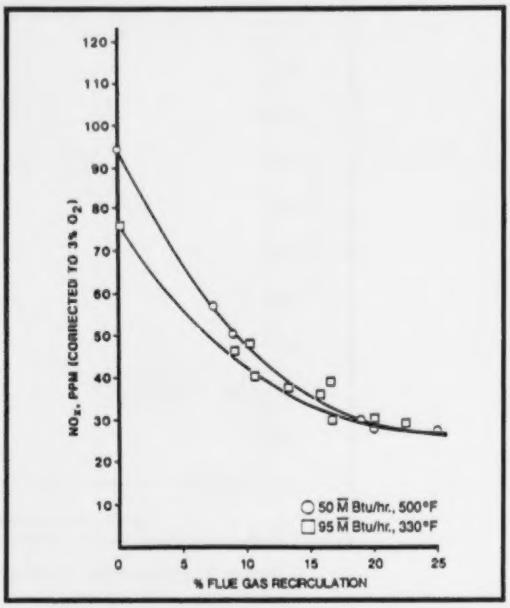


Figure 5: Staged Fuel Burner:
NO_x vs. FGR (2% O_2, 330°F and 500°F)

References

1. Waibel, R., et al., "Fuel Staging Burners for NO_x Control", 1986 Symposium on Industrial Combustion Technologies, Chicago, Illinois.

2. Martin, R. R., "Burner Design Parameters for Flue Gas NO_x Control", John Zink Internal Report, 1981.

3. Gerdes, Jr., J. H., "AVC Test with FGR", John Zink Internal R&D Report, July 1988.

4. Gerdes, Jr., J. H., "AVC Test with Preheated Air", John Zink Internal R&D Report, December 1988.

ENGINEERING EVALUATION OF COMBINED NO_x/SO_2 REMOVAL PROCESSES: INTERIM REPORT

W. DePriest
Project Manager
Sargent & Lundy
Chicago, Illinois

J. B. Jarvis
Senior Chemical Engineer
Radian Corporation
Austin, Texas

J. E. Cichanowicz
Project Manager
Electric Power Research
Institute
Palo Alto, California

ABSTRACT

In recent years, international pressures for strict control of NO_x emissions have rivaled those historically directed at SO_x. Japan has required postcombustion NO_x control since the late 1970s and plans in Europe call for up to 30,000 MW of NO_x control capacity by 1990. Presently, the technology most often selected to achieve this control is selective catalytic reduction (SCR). These international developments may encourage U.S. regulatory agencies to consider some level of additional NO_x control for coal-, oil-, and gas-fired generation. This potential, in conjunction with the existing strict SO_2 control requirements, has renewed interest in the development of lower cost SO_x and NO_x control technologies.

Under Electric Power Research Institute (EPRI) Project RP 3004-1, Sargent & Lundy along with its subcontractor Radian has been commissioned to perform an investigation of combined NO_x/SO_x processes. The goal of this project is to identify lower cost alternatives to the separate technologies of SCR for NO_x control and conventional flue gas desulfurization (FGD) for SO_x control.

Preceding page blank

Over 60 combined NO_x/SO_x processes were identified at the project outset as potential candidates for application to the utility industry. These 60 processes can be placed in the following six categories:

- solid adsorption/regeneration processes,
- irradiation of the flue gas processes,
- wet scrubbing processes,
- gas/solid catalytic processes,
- electrochemical processes, and
- alkali injection processes.

This paper represents an interim progress report of this investigation with approximately 30% of the project completed.

INTRODUCTION

The increasing regulation of NO_x emissions in Europe and the stringent regulations in place in Japan for nearly 10 years may increase the pressure on U.S. regulatory agencies to promulgate some form of NO_x control on fossil-fueled power generation facilities here in the United States. Presently, selective catalytic reduction (SCR) for NO_x control and flue gas desulfurization for SO_2 control have the most widespread use in both Europe and Japan. However, this combination has some significant shortcomings, primarily the very limited experience with SCR on high-sulfur fuels and the combined costs for both technologies.

An in-depth technical and economic understanding of potential alternatives to SCR and FGD by the utility industry could identify a minimum cost control strategy for NO_x and SO_2 emissions. If the utility industry can identify the most cost-effective alternate technologies and implement a development program to bring these technologies to commercial feasibility, then they may be able to minimize the capital investment and effect on plant efficiency typically associated with controlling NO_x and SO_2.

Another major motivation for this study is to reduce the process supplier's uncertainty in applying their technology to the power industry. This study will identify weaknesses in the processes to help focus future development expenditures and ultimately reduce the risk to the suppliers and the users.

Over 60 combined NO_x/SO_2 processes were identified at the project outset as potential candidates for application in the utility industry. The goal of this project is to select the most promising processes from these candidate processes to meet specific criteria of interest to utility power generators. We will also identify what additional development work will be necessary to reduce any perceived risk associated with the selected process technologies.

DESIRABLE FEATURES

To facilitate the comparison of these combined NO_x/SO_2 processes with SCR and FGD, six desirable features have been identified as follows:

- low/modest capital cost,
- low/modest operating cost,

- reliability,
- capability to follow turndown and load swings accompanying cycling plants,
- minimum long-term environmental risk, and
- broad applicability within the power industry.

PROJECT APPROACH

The project approach for evaluating alternate technologies for controlling both NO_x and SO_2 has been organized into six major tasks.

Screening Methodology (Task 1)

In this task a methodology was developed for selecting, from a population of over 60, approximately eight processes for detailed evaluation in later tasks. The number of processes actually selected may vary depending on the outcome of this screening methodology. This methodology has been designed to consider both the desirable features of a process from a utility's operating perspective and the applicability of each process for a given plant design and environmental control requirements. This task has been completed, and details of the methodology are presented in the Interim Results section of this paper.

Process Information (Task 2)

This task consisted of gathering the necessary data from the process designers to support the questions asked by the screening methodology developed in Task 1. This task is nearly complete with information continuing to be received from some of the process suppliers.

Process Selection (Task 3)

This task involves the application of the Task 1 methodology using the Task 2 information. This task is currently underway, and the eight final process technologies should be identified by April 1989.

Preliminary Assessment and Process Economics (Task 4)

The objective of this task is to develop specific designs for each of the eight processes and use the results in a technical feasibility and cost analysis. An important component of this task will be establishing critical design premises that define a consistent and fair basis for evaluating and comparing the eight processes. Based on these criteria, a conceptual engineering design (flow sheets, P&IDs, major equipment list, consumables, and O&M and capital costs) will be developed and used to identify effects on plant heat rate, reliability, and balance-of-plant costs for each process. This activity is scheduled to begin in April 1989 and end in August 1989.

Sensitivity Analyses (Task 5)

The sensitivity of the individual process costs to variations in the critical design premises and economic parameters will be studied in this task scheduled for the latter part of 1989.

Research and Development (Task 6)

In this task the development needs for each process will be assessed. These development needs may be directed towards research required to bring the process to commercial viability or research that will simplify the process design and/or improve the economics.

SCHEDULE

The duration of the project is 24 months with a start date of May 1988.

INTERIM RESULTS

Highlights of the activities completed to date are summarized as follows.

Preliminary Screening Methodology

The starting point for this project was a planning study conducted for EPRI by Battelle that identified 58 processes as potential candidates for combined NO_x/SO_2 control. An additional seven processes were identified through other sources. To reduce the number of processes to a more manageable level, a preliminary screening process was initiated. Each of the 65 process developers was contacted by telephone or letter. The objective was to determine the operation of the process and obtain initial information about the operation of the process. In order to continue in the evaluation, processes had to meet the following minimum requirements:

- Some degree of experimental development had to have occurred on the process. That is, purely conceptual processes were eliminated from the evaluation.
- Some level of development had to have occurred within the last 5 or so years. Processes inactive for longer than this were considered abandoned.
- Process developers had to be willing to provide additional information on the process needed for evaluation.
- Processes had to be applicable to controlling emissions from coal-fired boilers. Some processes, either as a result of the reagent used (e.g., high cost or limited availability) or the type of processing required, were judged to be better suited for use in other industries or smaller applications and, therefore, not applicable to the utility industry.

The above approach yielded 28 process developers engaged in research on various NO_x/SO_2 processes. These developers represent 18 clearly defined technologies and 24 processes that have differences significant enough to warrant separate evaluation.

Process Categorization

To facilitate the qualitative evaluation, processes meeting the preliminary screening requirements were sorted into categories based on process type. Six categories resulted, and the processes assigned to each category are listed in Table 1. A brief description of the six categories, including the ultimate "fate" of both the NO_x and SO_2 as well as some of the advantages and disadvantages follows.

Solid Adsorption/Regeneration. The processes in this first category lead to the following results:

- fate of SO_2 - sulfuric acid, sulfur, or liquified SO_2; and
- fate of NO_x - reduction to nitrogen.

TABLE 1

PROCESSES UNDER CONSIDERATION FOR COMBINED NO_x/SO_2 CONTROL

Overall Process Group	Process Name
Solid Adsorption/Regeneration	UOP/PETC Fluidized-Bed Copper Oxide Process Rockwell Moving-Bed Copper Oxide Process NOXSO Process Mitsui/BF Activated Coke Process Sumitomo/EPDC Activated Char Process Sanitech Nelsorbent SO_x/NO_x Control Process
Irradiation of the Flue Gas	Ebara E-Beam Process Karlsruhe Electron Streaming Treatment ENEL Pulse-Energization Process CE Pulsed Streamer Corona Process Concord UV SO_x/NO_x Control Process
Wet Scrubbing	Saarberg-Holter Iron Chelate Scrubbing Argonne/Dravo ARGONNOX Process Dow Electrochemical Regeneration Process Dow Polychelant/Ultrafiltration Process PETC Electrodialysis Process California (Berkeley) Ferrous Cysteine Process
Gas/Solid Catalytic Operations	Haldor Topsoe WSA-SNO_x Process Degussa DESONOX Process B&W $SO_x/NO_x/RO_x/BO_x$ (SNRB) Process Parsons Flue Gas Cleanup Process Lehigh University Low-Temperature SCR Process
Electrochemical Operations	IGR/Helipump Solid-State Electrochemical Cell
Alkali Injection Operations	Argonne High-Temperature Spray Drying Studies PETC Mixed Alkali Spray Dryer Studies Batelle ZnO Spray Dryer Process

The processes in this category use a recirculating solid sorbent material to remove SO_2 and NO_x from the flue gas. Sorbents used for this purpose include activated carbon or coke, alumina-based sorbents with additives such as copper oxide or sodium, and magnesium oxide-based sorbents.

In general, SO_2 is bound to the sorbent as sulfate and is released as either SO_2, or a mixture of SO_2, H_2S, or elemental sulfur, during regeneration in a reducing atmosphere. Typical reducing gases can include natural gas, hydrogen, carbon dioxide, or synthetic gas. The concentrated sulfur species released during regeneration can be treated to produce byproducts, which include sulfuric acid, liquified SO_2, or elemental sulfur.

All of the processes in this category ultimately reduce NO_x to nitrogen. However, the techniques to accomplish this vary. In some cases, NO_x is catalytically reduced in the adsorption step by adding a reducing agent such as ammonia to the flue gas. This approach is used with activated carbon or coke sorbents and in processes utilizing copper oxide. In other processes, NO_x is absorbed from the flue gas and reduced during sorbent regeneration. In one process, absorbed NO_x is released by heating the sorbent before adding the reducing gas. The desorbed NO_x is then recycled to the boiler where a portion of it reportedly will be reduced to N_2 within the burner flame zone. A steady-state NO_x concentration within the furnace is achieved that is somewhat higher than the original NO_x concentration.

A contacting device is required to mix the flue gas and the sorbent. Typical approaches involve the use of a fluidized or moving bed of the sorbent material. Spent sorbent is continuously removed from the absorber, regenerated, and then returned to the absorber vessel.

The processes differ in terms of the temperature regime in which they can be applied. Copper oxide sorbents operate at about 700°F. Therefore, access to the flue gas stream is required upstream of the air heater. Regeneration of the copper oxide sorbent occurs at slightly higher temperatures. Other sorbents can be used at lower temperatures (below 300°F) and can be applied downstream of the air heater and/or particulate collection device. However, the required regenerator temperature is typically much higher (above 1000°F).

One of the major operating concerns for these processes is sorbent attrition. Sorbent makeup costs can be high and are aggravated by the transport of solids between and within the adsorption/regeneration steps.

Solid adsorption/regeneration processes have these primary advantages:

- most processes are capable of high SO_2 and NO_x removal levels;
- the processes produce no large waste streams or sludges;
- the processes can produce a potentially marketable byproduct such as sulfuric acid, sulfur, or concentrated SO_2; and
- flue gas reheat is not typically required.

Solid adsorption/regeneration processes have these primary disadvantages:

- sorbent recirculation of hot solids is a mechanically complex operation;
- sorbent attrition (or consumption) may be a significant operating cost;
- flue gas pressure drops through the reactor and subsequent particulate collections device (if required) can be high; and
- processes utilizing a fluidized bed or having a significant temperature differential between the adsorption/regeneration steps may have limited turndown capability.

Irradiation of the Flue Gas. The processes in this second category lead to the following results:

- fate of SO_2 - ammonium sulfate or dry calcium sulfite/sulfate solids, and
- fate of NO_x - ammonium nitrate or dry calcium nitrate solids.

Irradiation of the flue gas can be used to produce reactive intermediates that subsequently oxidize SO_2 and NO_x to their respective acids. In most cases, ammonia is added upstream of the reactor so that ammonium sulfate and nitrate solids are formed. These processes are applied following particulate control so that the ammonium compounds can be used as fertilizers. A second particulate control device is required to collect the dry ammonium salts.

The most developed process in this group utilizes electron accelerators that provide high-energy electrons to the flue gas. There are, however, several other techniques that have been investigated for irradiating the flue gas. For example, an electrical pulse can be used to develop a corona discharge in a reactor that has a configuration similar to an electrostatic precipitator (ESP). The electrons generated during the pulse serve the same function as those generated by an electron generator. Other techniques for irradiating the flue gas include the use of microwave and ultraviolet radiation.

In general, irradiation processes operate in a temperature range between 150° and 200°F. Therefore, some cooling of the flue gas leaving the air heater is required to reach the optimum temperature range.

Processes employing irradiation of the flue gas have the following primary advantages:

- SO_2 and NO_x are controlled simultaneously in a single step for which high removal levels can be obtained (at the expense of higher power consumption);
- processes do not produce a high-volume waste stream;
- processes produce a potentially salable byproduct (ammonium sulfate and nitrate) that could be used as a fertilizer;
- processes should have good load following characteristics; and
- processes are suitable for retrofit application because access to high-temperature flue gas is not required.

Processes employing irradiation of flue gas have the following primary disadvantages:

- process energy requirements are high;
- equipment for irradiating the flue gas is not yet available in sizes required for application to utility boilers; and
- the potential exists for emissions of ammonia, sulfuric acid, and nitrous oxide (N_2O).

Wet Scrubbing. The processes in this third category lead to the following results:

- fate of SO_2 - calcium sulfite/sulfate sludge or ammonium sulfate, and
- fate of NO_x - conversion to nitrate and nitrogen-sulfur salts or nitrogen.

Wet scrubbing processes can be used to absorb both SO_2 and NO_x from flue gas. Due to the low solubility of NO, however, special measures must be taken. These include oxidation of NO to NO_2 in either the gas or liquid phase, or the use of additives to increase the solubility of NO.

The first group of processes utilize an oxidant such as ozone, chlorine dioxide, or hydrogen peroxide to oxidize NO to NO_2. NO_2 is more soluble than NO and reacts to form nitrite and nitrate in the scrubbing liquor. Nitrite then reacts with dissolved sulfite to form soluble sulfur-nitrogen compounds such as hydroxylamine disulfonate (HADS). The principal drawbacks to this approach include the high cost and hazardous nature of the oxidants and the generation of a waste stream containing the soluble nitrogen salts (nitrate and sulfur-nitrogen species). When chlorine dioxide is used as the oxidant, the waste stream also contains chloride.

The second group of processes utilize an additive to increase the solubility of NO. These additives include iron chelates such as iron EDTA, along with a variety of other materials capable of forming complexes with NO. The iron-chelate-NO complex can react with dissolved sulfite or other reducing agents to form a regenerated iron chelate, nitrogen, and sulfur-nitrogen compounds such as HADS. The drawbacks to this approach include oxidation of Fe^{+2} to inactive Fe^{+3}, generation of a waste stream containing soluble nitrogen-containing reaction products, and high chelate consumption due to losses in the blowdown stream.

Development work on the iron-chelate processes has centered on techniques to maintain iron in the active +2 form and to separate the iron chelate from the dissolved sulfur and nitrogen salts in the blowdown stream. These methods include electrochemical regeneration of the iron (+3), and electrodialysis and filtration techniques to minimize losses of the iron-chelate.

Both of the approaches described above are enhanced by elevated dissolved sulfite concentrations in the absorption liquor. In the first case, sulfite helps to absorb and react with NO_2. In the second case, sulfite is required to reduce the iron-chelate-NO complex and also reduces a portion of the inactive iron (+3). In order for sufficient sulfite to be present, the amount of SO_2 absorbed from the flue gas must exceed (by roughly a factor of two) the amount of NO_x removed. Therefore, these processes are better suited to high-sulfur fuels.

The fate of absorbed SO_2 depends on the type of chemistry employed in the process. Since high dissolved sulfite is desirable, sodium-based (dual alkali), magnesium-enhanced lime/limestone, or ammonia-based scrubbers could be utilized. The lime/limestone and dual alkali chemistries produce a calcium sulfite/calcium sulfate waste sludge unless gypsum is produced via forced oxidation. An ammonia-based process, utilizing oxidation with ozone, could be used to produce ammonium sulfate and nitrate. However, the product could be contaminated with sulfur-nitrogen species, which might lessen its value as a fertilizer.

The primary advantages of wet scrubbing processes include the following:

- processes could be applicable as retrofits to some existing wet FGD systems;
- SO_2/NO_x removal can be obtained in a single vessel; and
- processes are suitable for high-sulfur systems.

The primary disadvantages of wet scrubbing processes include the following:

- processes use complex chemistries or employ hazardous reagents (ozone or chlorine dioxide);
- processes produce a liquid waste containing soluble nitrogen species (treatment of this stream will increase operating costs); and
- high levels of NO_x removal may not be obtainable using existing FGD system contactor designs.

Gas/Solid Catalytic Operations. The processes in this fourth category lead to the following results:

- fate of SO_2 - sulfuric acid or sulfur, and
- fate of NO_x - reduction to nitrogen.

The processes in this category use a fixed catalyst bed (or beds) to remove SO_2 and NO_x from the flue gas. Typically, the processes employ a catalyst bed that has a design similar to that used for selective catalytic reduction (SCR). In general, the processes operate at elevated temperatures and therefore require access to flue gas before the air heater.

The fate of NO_x is the same for all of these processes and involves the reduction of NO_x to nitrogen. Reducing agents such as natural gas, ammonia, or synthetic gas are used for this purpose. The fate of SO_2 varies, depending on the process, with both sulfuric acid and sulfur as potential byproducts. No large volume waste streams are generated in any of the processes.

Several of these processes use two catalytic reactors. In the first reactor, NO_x is reduced to nitrogen using ammonia injection and an SCR catalyst. In the second reactor, SO_2 is catalytically oxidized to sulfuric acid. The sulfuric acid is then condensed to give a salable byproduct. These processes are considered combined SO_2/NO_x processes because the presence of the SO_2 oxidation catalyst allows the SCR reactor higher levels of ammonia slip than in conventional SCR systems. Ammonia leaving the SCR reactor is subsequently oxidized to NO_x in the second catalytic reactor. While this slightly decreases the net NO_x removal capability of the process, ammonia emissions are eliminated along with the potential for ammonium sulfate deposit formation downstream of the second reactor.

Another process is under development in which an SCR catalyst is located inside the bags of a hot baghouse. Upstream of the baghouse, alkali is injected into the flue gas to remove SO_2. This generates a calcium- or sodium-based waste stream. Ammonia is also injected upstream of the baghouse to promote NO_x removal in the SCR catalyst. Prior removal of most of the SO_2, along with particulates, may simplify the operation of the SCR catalyst.

Development is proceeding on a process that uses a catalyst to reduce both NO_x and SO_2 (to nitrogen and H_2S). In this process, the H_2S is recovered and converted to sulfur.

Finally, catalysts are being developed that may accomplish selective catalytic reduction of NO_x at lower temperatures. The goal is to develop a process that can be applied more easily as a retrofit to existing boilers.

Gas/solid catalytic processes have these primary advantages:

- processes use fixed-bed reactors that do not require circulation of solid sorbents;
- high removal levels of SO_2 and NO_x are possible;
- most of these processes can produce a potentially valuable by-product with no large waste streams; and
- stack gas reheat is not typically required.

Gas/solid catalytic processes have these primary disadvantages:

- most processes operate at elevated temperature (which in retrofit applications would require access to flue gas upstream of the air heater);
- the potential exists for secondary air emissions of species such as ammonia, sulfuric acid mist, and H_2S;
- some of these processes require the collection and concentration of dilute quantities of SO_3 or H_2S from the flue gas, which increases the mechanical complexity of the process; and
- catalysts may be deactivated by components in the flue gas, which could necessitate periodic regeneration or replacement of portions of the catalyst bed.

Electrochemical Operations. The processes in this fifth category lead to the following results:

- fate of SO_2 - sulfur or sulfuric acid, and
- fate of NO_x - reduction of nitrogen.

A number of electrochemical processes have been proposed for the removal of SO_2. (Electrochemical potential can be used to either reduce SO_2 to sulfur or oxidize it to sulfuric acid.) However, only one process has so far demonstrated the capability for combined SO_2/NO_x removal. This process uses a solid-state electrolytic cell with a ceramic electrolyte. In the cathodic zone of the cell, electrochemical reduction of SO_2 and NO_x yields sulfur, nitrogen, and oxygen ions (which dissolve in the solid electrolyte). At the anode, oxide ions are converted to oxygen gas. All three products--sulfur, nitrogen, and oxygen--remain in the flue gas. Sulfur would be condensed downstream and sold as a byproduct. The process is still in the early stages of development, and it is not yet clear how the process would be applied at a coal-fired boiler. However, the cell operating temperature appears to be in the range of 850°F to 950°F.

Processes employing electrochemical operations have the primary advantages:

- they are mechanically simple processes;
- SO_2 and NO_x are removed simultaneously;
- no water, reagents, or other materials are required; and
- elemental sulfur is produced as a byproduct with no other waste streams being generated.

Processes employing electrochemical operations have these disadvantages:

- sulfur recovery may be difficult because of the low sulfur concentration in the flue gas;
- electrical requirements may be relatively high;
- processes operate at high temperature, which complicates retrofit applications; and
- process is in early stage of development.

Alkali Injection. The processes in this sixth category lead to the following results:

- fate of SO_2 - dry calcium or sodium-based solid waste, and
- fate of NO_x - conversion to nitrogen and soluble nitrate or sulfur-nitrogen compounds.

Several processes have been proposed that use alkali injection to remove SO_2 from flue gas. If an additive containing sodium is included, NO_x removal can also be obtained. Reportedly, sodium sulfite acts as a catalyst to oxidize NO to NO_2, which can react with sulfite to form nitrogen, nitrates, or sulfur-nitrogen compounds.

One process utilizing this approach involves the use of a spray dryer at a higher than normal spray dryer temperature of around 200°F. A sodium additive, such as sodium hydroxide, is added to the lime slurry fed to the spray dryer. NO_x removal is optimized (at about 50% removal) at the higher operating temperature. However, SO_2 removal decreases somewhat as the temperature is increased. Test results show that most of the NO_x removal occurs across the filter cake in the baghouse.

A second approach, useful for lower sulfur applications, involves dry injection of sodium compounds (e.g., sodium bicarbonate) into the flue gas leaving the air heater. Due to NO oxidation, however, NO_2 concentrations may actually increase, and can result in the formation of a visible, and therefore undesirable, brown plume. Similar increases in NO_2 levels have also been observed with the high-temperature spray dryer approach. Test results have demonstrated that injection of ammonia or urea with the sodium sorbent can reduce the tendency for plume coloration.

Processes employing alkali injection have the following primary advantages:

- processes are suitable for relatively inexpensive retrofit applications (e.g., existing spray dryers may be modified to operate in the NO_x removal mode); and
- processes operate at relatively low temperatures (access to flue gas upstream of the air heater is not required).

Processes employing alkali injection have the following primary disadvantages:

- NO_x removals are relatively low (less than about 50%) and high SO_2 removals (greater than 90%) may be difficult to obtain when NO_x removal is maximized;
- the potential exists for increased NO_2 emissions and the formation of an undesirable brown plume, although this problem may be minimized by injection of ammonia or urea; and
- the dry solid waste stream contains soluble sodium compounds, which could present some waste disposal problems and limit the application of these processes at some existing utilities.

Qualitative Screening Methodology

A detailed methodology has been developed to select the eight "best" processes for more detailed evaluation.

A direct comparison of all 28 processes is not possible as each process differs in its capability to remove NO_x and SO_2 and its applicability to existing plants (retrofit) and new plants. Accordingly, three application categories for the NO_x/SO_2 processes have been defined to enable a direct comparison between and among relevant processes.

These application categories are defined as follows:

- Near-term processes suitable for retrofit applications. Processes in this category will be at or near a commercial status and will be amenable to retrofitting within an existing plant site. As these processes are primarily for retrofit application, extremely high NO_x and SO_2 removal (e.g., 90%) may not be necessary, consistent with the anticipated form of the possible acid rain legislation.
- Near-term processes suitable for new plant applications. Processes within this category will be at or near a commercial status and will be suited for new plants where site constraints are minimal. These processes will likely be required to meet high NO_x and SO_2 removal consistent with present and anticipated revisions to NSPS requirements.
- Long-term processes where significant research and development are required to achieve commercial status. Accordingly, these processes may not be available for full scale use within the next 10 years. Processes in this category will most likely be limited to those that can achieve the high removal necessary for NSPS. However, processes that appear to be capable of achieving the removal necessary to meet anticipated acid rain legislation requirements within the anticipated time restraints will also be included.

Since exact cost information is not available, a qualitative ranking will be used to select the most promising processes. The qualitative ranking is based on the desirable features listed in the beginning of this paper.

Several criteria were developed to qualitatively define these desirable features and to allow a comparison to conventional state-of-the-art SCR and FGD technologies. For example, criteria that can be used to assess reliability include mechanical and chemical process complexity, tolerance to fly ash, and the presence of corrosive environments.

The processes being considered for combined SO_2/NO_x control show considerable variation in terms of these desirable features. With respect to costs, many of the processes that produce a salable by-product have relatively high capital costs due to the equipment required to collect, purify, and store the by-product. However, these by-products can potentially be sold to offset operating costs. Alternatively, while the wet scrubbing and alkali injection processes may offer lower capital costs, these processes produce a sludge or solid waste product that must be disposed of. Furthermore, these waste streams may constitute a long-term environmental risk.

Similar trade-offs are evident for the other desirable features. For example, the solid absorption/regeneration processes typically operate at a low temperature (which increases their applicability) and produce no large waste streams (which minimizes long-term environmental risk). However, these processes require circulation of the hot solid sorbent, which can adversely affect the reliability and load-following capabilities of these processes. In contrast, the gas/solid catalytic processes operate at higher temperatures, which decreases their general applicability for retrofit applications. However, these processes are mechanically less complex (which should result in better reliability) and may be better able to follow load changes than the solid absorption/regeneration processes.

The process-developer-supplied information and engineering judgment on the part of the project team will be used to give each process a score for each criterion under each desirable feature. This score will represent the reviewer's opinion on the impact that each criterion has on the desirable feature compared to SCR/FGD.

For the cost-related desirable features, crude cost estimates will be prepared. These crude cost estimates will, in all likelihood, be based on limited information. However, a relative ranking among the processes will result.

The relative importance of each criterion will be considered by weighting each of the criteria under each desirable feature. In addition, the relative importance of each desirable feature can be weighted. The resulting score for each process will be determined by summing the weighted scores for each criterion under each desirable feature. The framework for managing the qualitative evaluation has been developed using a spreadsheet; however, the assignment of specific weighting factors has been delayed until additional information on each process has been obtained. The spreadsheet approach will allow sensitivity analyses to account for the effects of alternative future utility environments.

SUMMARY

This project is approximately 30% complete and although no conclusions as to the feasibility of these processes are clearly apparent, major steps have been taken to achieve this goal. Research into the background and status of these processes have allowed us to eliminate some of the processes and categorize the remaining ones into similar process groups. We have also identified application categories to encompass the forecasted emission scenarios for both new and retrofit power generation facilities. These process categories and application categories will facilitate matching the processes' respective capabilities (removal efficiency, retrofitability, and status of development) with a range of applications and ultimately facilitate a fair and equitable relative evaluation of the processes.

Future project activities will select and study in detail the eight most promising processes capable of achieving reliable and low cost NO_x and SO_2 control.

REFERENCES

Numerous sources (technical bulletins, product brochures, written correspondence, telecons, etc.) of information were used in the preparation of this interim report on the evaluation of combined NO_x/SO_2 removal processes. Readers of this report should be aware that any conclusions presented in this report are preliminary and subject to change as more definitive information is gathered from the process developers. Specific reference information is available upon request.

Appendix A

EPRI/EPA Symposium on Stationary Combustion NOx Control

03/06/89-03/09/89

San Francisco, CA

List of Attendees

James R. Adams
Project Manager
New York State Electric & Gas
4500 Vestal Parkway, East
Binghamton, NY 13903
607/724-0849

Rui Afonso
Senior Research Engineer
New England Electric System
25 Research Drive
Westborough, MA 01582
508/366-9011

Ken Ahn
N/A
Coen Company
1510 Rollins Road
Burlingame, CA 94010
415/697-0440

Charles D. Allen
Sr. Mechanical Consulting Engr.
Arizona Public Service Company
P.O. Box 53999
Phoenix, AZ 95072-3999
602/371-6750

Sy B. Alpert
EPRI Fellow
Electric Power Research Institute
3412 Hillview Avenue
Palo Alto, CA 94304
415/855-2512

Leonard C. Angello
Project Manager
Electric Power Research Institute
3412 Hillview Avenue
Palo Alto, CA 94304
415/855-2873

James A. Armstrong
Vice President, Operations
ADA Technologies, Inc.
304 Inverness Way South, Suite 480
Englewood, CO 80112
303/792-5615

D. S. Arnold
Engineering Specialist
Kerr-McGee Corporation
P.O. Box 25861
Oklahoma City, OK 73125
405/270-2911

Wayne J. Aronson
Chief, Program Support Section
U.S. EPA
345 Courtland Street
Atlanta, GA 30365
404/347-2864

Patrick F. Aubourg
Supervisor
Owens Corning Fiberglas
Tech. Center, P.O. Box 415
Granville, OH 43023
614/587-7604

A. Baldacci
Senior Engineer
ENEL
Via G. B. Martini 3
00198 Rome, ITALY
6/8509-2898

Lothar Balling
Dipl.-Ing.
Siemens AG, KWU Group
Hammerbacherstrasse 12+14
D-8520 Erlangen
FEDERAL REPUBLIC OF GERMANY
9131/182350

Joe Barsin
Manager, Industrial Projects
Babcock & Wilcox
20 S. Van Buren Avenue
Barberton, OH 44203
216/860-1552

Dwayne Bateson
Executive Assistant
TransAlta Utilities
110 12th Avenue, S.W.
Calgary, Alberta T2P 2M1
CANADA
403/267-7129

Nick Bayard de Volo
President
Energy Technology Consultants
2091 Business Center Drive
Suite 100
Irvine, CA 92715
714/833-2522

Peter R. Beal
Manager, Business Development
NEI International Combustion, Ltd.
Sinfin Lane
Derby DE2 9GJ
UNITED KINGDOM
332/271111

Gordon Beales
Project Manager
Electric Power Research Institute
3412 Hillview Avenue
Palo Alto, CA 94304
415/855-2591

Rob Becker
President
Environmental Catalyst Consultants
P.O. Box 637
Spring House, PA 19477
215/628-4447

Joseph Beer
Department Manager
Siemens AG, KWU Group
Hammerbacherstrasse 12+14
Dept. U3112, 8520 Erlangen
FEDERAL REPUBLIC OF GERMANY
09131/182932

Ted Behrens
Account Executive
Fuel Tech
61 Taylor Reed Place
Stamford, CT 06906
203/359-1320

Gerald R. Bemis
Engineer
California Energy Commission
R&D Office
1516 9th Street, MS-43
Sacramento, CA 95814-5512
916/324-3468

Angelo Benanti
Mgr., Thermal Equipment
ENEL
Via G. B. Martini 3
00198 Rome, ITALY
6/8509-2898

Knud Bendixen
Vice President
Burmeister & Wain Energy
23 Teknikerbyen
Virum, DENMARK 2830
45/2 857100

Mogens Berg
N/A
Elkraft Power Company
5 Lautruphoej
DK-2750 Ballerup, DENMARK
45/2 660022

Leif Bernergurd
Technical Officer
Environment Protection Board
Box 1302
S-17125 Solna, SWEDEN
8/799-1119

Sisto Bertacchi
Senior Researcher
ENEL
Via A. Pisano 120
Pisa, ITALY 56100
050/535693

Gary L. Bisonett
Senior Engineer
Pacific Gas & Electric
245 Market Street, Room 434A
San Francisco, CA 94106
415/973-6950

Kerry Blamire
Generation Studies
Nova Scotia Power Corporation
P.O. Box 910
Halifax, Nova Scotia
CANADA B3J 2W5
902/428-6655

Verle Bland
Manager, Applied Technology
KVB, Inc.
9342 Jeronimo
Irvine, CA 92718
714/587-2326

Richard Boardman
Student
Brigham Young University
184 CB
Provo, UT 84602
801/378-2076

Richard T. Bobick
Senior Process Engineer
Unocal Corporation
1201 West 5th Street
P.O. Box 7600
Los Angeles, CA 90051
213/977-6435

Dieter Boekenbrink
Director
RWE
5180 Eschweiler, Box 1448
WEST GERMANY
02403-732112

Diego Bonolis
N/A
ENEL
Via G.B. Martini 3
00198 Rome, ITALY
06/85095192

Peter J. Booras
President
Yankee Energy Corporation
80 Boylston Street
Boston, MA 02116
617/542-0550

Richard W. Borio
Principal Consulting Engineer
Combustion Engineering
1000 Prospect Hill Road
Windsor, CT 06095
203/285-2229

Kerry W. Bowers
Senior Research Engineer
Southern Company Services
P.O. Box 2625
Birmingham, AL 53202
205/870-6825

Wallace H. Bradley
V.P., Engineering
Austell Box Board Corporation
P.O. Box 157
Washington Street
Austell, GA 30001
404/948-3100

Jan Brandin
N/A
University of Lund
Chemical Engineering II
P.O. Box 124
S-221 00 Lund, SWEDEN
046/108284

Ron L. Bredehoft
Staff Planning Analyst
Chevron U.S.A.
324 W. El Segundo Boulevard
El Segundo, CA 90245
213/615-5000

Bernard P. Breen
President
Energy Systems Associates
1840 Gateway Three
Pittsburgh, PA 15222
412/392-2380

Brent Brigham
Project Engineer
Unocal Corporation
P.O. Box 758
Wilmington, CA 90748
213/513-7600

R. G. Broderick
V.P. Engineering
Fuel Tech
61 Taylor Reed Place
Stamford, CT 06906
203/359-1320

W. J. Brooks
Senior Engineer
CEGB
Barnett Way, Barnwood
Gloucester GL4 7RS
UNITED KINGDOM
0452/652-306

Bert Brown
Applications Manager
Joy Technologies, Inc.
404 E. Huntington Drive
Monrovia, CA 91016-3633
818/301-1172

Douglas R. Brown
Engineer
Applied Utility Systems
1140 E. Chestnut Avenue
Santa Ana, CA 92701
714/953-9922

Gordon Brown
Staff Engineer
Exxon Chemical Americas
5000 Bayway Drive
Baytown, TX 77522
713/425-5033

C. P. Brundrett
Manager
W. R. Grace & Company
10 E. Baltimore Street
Baltimore, MD 21202
301/659-9125

Mark R. Burkhardt
Research Chemist
ADA Technologies, Inc.
304 Inverness Way South, Suite 480
Englewood, CO 80112
303/792-5615

Kenneth R. Burns
Product Manager
Engelhard Corporation
Edison, NJ 08818
201/632-6640

Tony A. Burns
V.P. & Mgr., Env. Technology Group
S-Cubed, Division of Maxwell Labs
P.O. Box 1620
La Jolla, CA 92038
619/453-0060

John W. Byrne
Senior Research Chemist
Engelhard Corporation
Menlo Park
Edison, NJ 08818
201/321-5153

Scott Cameron
Sales Engineer
Babcock & Wilcox
17172 Abalone Lane, #207
Huntington Beach, CA 92649
714/846-0817

Gary A. Camody
Product Services Manager
Combustion Engineering
1000 Prospect Hill Road
Windsor, CT 06095
203/285-5039

E. J. Campobenedetto
Marketing Manager
Babcock & Wilcox
20 S. Van Buren Avenue
Barberton, OH 44203
216/860-6762

Giovanni Caprioglio
Consultant
General Atomics
P.O. Box 85608
San Diego, CA 92138-5608
619/455-2918

E. J. Capriotti
Vice President, Sales
Fuel Tech
61 Taylor Reed Place
Stamford, CT 06906
203/359-1320

James Carnevale
Supervising Mechanical Engineer
Los Angeles Dept. of Water & Power
P.O. Box 111, Room 604
Los Angeles, CA 90051
213/481-4895

Baldwin K. Chan
Sr. Mechanical Engineer
Pacific Gas & Electric
77 Beale St., Room 2523
San Francisco, CA 94106
415/972-5236

Charles Chang
Assistant Supervisor, Air Quality
Los Angeles Dept. of Water & Power
111 N. Hope Street
Los Angeles, CA 90012
213/481-3235

Shih-Ger Chang
Senior Scientist
Lawrence Berkeley Laboratory
University of California
Berkeley, CA 94720
415/486-5125

Wei-Yin Chen
Assistant Professor, Research
Louisiana State University
Department of Chemical Engineering
Baton Rouge, LA 70803
504/388-3059

Lisa J. Chrisman
Engineer
Fossil Energy Research Corporation
821 Hamilton Drive
Pleasant Hill, CA 94523
415/937-9007

Roger C. Christman
Program Manager
Radian Corporation
13595 Dulles Technology Drive
Suite 200
Herndon, VA 22071
703/834-1500

Ed Cichanowicz
Project Manager
Electric Power Research Institute
3412 Hillview Avenue
Palo Alto, CA 94304
415/855-2374

Leonard Clayton
Field Engineering
Bay Area Air Quality Mgmnt. Dist.
939 Ellis Street
San Francisco, CA 94109
415/771-6000

Robert J. Collette
Contract Manager
Combustion Engineering
1000 Prospect Hill Road, 5034-GC25
Windsor, CT 06095-0500
203/285-5687

Roger S. Cook
Environmental Engineer
Dept. for Environmental Protection
Kentucky Div. for Air Quality
18 Reilly Road
Frankfurt, KY 40601
502/564-3382

Frederick M. Coppersmith
Manager, Research & Development
Con. Edison Co. of New York
4 Irving Place
New York, NY 10003
212/460-3098

David A. Cowdrick
Senior Engineer
Tampa Electric Company
P.O. Box 111
Tampa, FL 33601
813/671-3361

Ed Cowle
Project Engineer
Bechtel Power Corporation
12440 E. Imperial Highway
Norwalk, CA 90650
213/807-2423

Anthony Cowley
Mechanical Design Supervisor
B. C. Hydro
970 Burrard Street
Vancouver, British Columbia
V6Z 1Y3
604/663-2849

William R. Cress
Manager, Engineering Studies
Allegheny Power Service Corporation
Cabin Hill Drive
Greensburg, PA 15601
412/838-6721

Diane V. Croson
Mgr., LLW/NOx Process Dev.
Westinghouse Idaho Nuclear Company
P.O. Box 4000
Idaho Falls, ID 83403
208/526-3402

Michael Davidson
Mgr., New Product Development
Combustion Engineering
1000 Prospect Hill Road
Windsor, CT 06095
203/285-9005

Charles B. Davis
Senior Staff Engineer
Virginia Power
5000 Dominion Boulevard
Glen Allen, VA 23060
804/273-2619

Gerard G. De Soete
Dr. es Sciences
Institut Francais du Petrole
1-4, Avenue de Bois-Preau
Box N311, 92506 Rueil-Mailmaison
Cedex, FRANCE
331/47526145

Dennis D. Delaney
Senior Research Chemist
Unocal Corporation
376 S. Valencia Avenue
Brea, CA 92621
714/528-7201 X2184

Mukesh S. Desai
Engineering Specialist
Bechtel Power Corporation
15740 Shady Grove Road
Location 2A-12
Gaithersburg, MD 20877-1454
301/258-3150

Dilip Deshpende
Supervising Engineer
Alberta Power Company
10035 105th Street
Edmonton, Alberta
CANADA D5G 2V6
403/420-7177

William DePriest
Project Engineer
Sargent & Lundy
55 E. Monroe Street
Chicago, IL 60603
312/269-6678

Bill Dick
Design Specialist
Ontario Hydro
700 University Avenue
Toronto, Ontario
CANADA M5G 1X6
416/592-8593

Maurizio Didio
N/A
Snamprogetti Spa
c/o Snamprogetti USA, Inc.
666 5th Floor
New York, NY 10103
212/399-1090

Richard Diffenbach
N/A
U.S. Department of Energy
P.O. Box 10940
Pittsburgh, PA 15236
412/892-6090

David J. Dodd
Mgr., Chemical Research
Ontario Hydro
800 Kipling Avenue
Toronto, Ontario
CANADA M8Z 5S4
416/231-4111 X6519

Roger Dodds
Air Quality Engineer
Wisconsin Electric Power Company
333 W. Everett Street
Milwaukee, WI 53201
414/221-2174

Zambelli Donato
Engineer
Azienda Servizi Municipal
Via. Lamarmora N. 230
Brescia, ITALY
030/3311-291

Yogesh P. Doshi
Senior Environmental Engineer
New Jersey Dept. of Env. Protection
401 E. State Street, 2nd Floor
Trenton, NJ 08625
609/633-7249

Dennis C. Drehmel
Technical Manager
U.S. EPA
AEERL -- MD-04
Research Triangle Park, NC 27711
919/541-7505

Joseph R. Dulovich
Plant Superintendent
Ohio Edison Company
1047 Belmont Avenue
Niles, OH 44446
216/544-7327

Michael K. Dunbar
Mechanical Engineer
Pacific Gas & Electric
77 Beale Street, Room 2547
San Francisco, CA 94106
415 972-0606

Richard A. Dye
Fossil Energy Department
U.S. Department of Energy
FE-4, Forrestal
Washington, DC 20585
202/252-6499

Owen W. Dykema
President
Dykema Engineering
5850 Canoga Avenue, Suite 400
Woodland Hills, CA 91367
818/712-0070

William C. Eddins
Dir., Division of Air Quality
Dept. for Environmental Protection
18 Reilly Road
Frankfurt, KY 40601
502/564-3382

Greg Eirschele
Environmental Engineer
Wisconsin Power & Light Company
222 W. Washington Avenue
Madison, WI 53701
608/252-3084

John W. Eldridge
Professor of Chemical Engrng.
University of Massachusetts
39 Kendrick Place
Amherst, MA 01003
413/253-5991

Tom E. Emmel
Mgr., Combustion Engineering Dept.
Radian Corporation
P.O. Box 13000
Research Triangle Park, NC 27709
919/541-9100

Robert Epperly
Executive Vice President
Fuel Tech
61 Taylor Reed Place
Stamford, CT 06906
203/359-1320

David Eskinazi
Project Manager
Electric Power Research Institute
3412 Hillview Avenue
Palo Alto, CA 94304
415/855-2918

Tony Facchiano
N/A
Coen Company
1510 Rollins Road
Burlingame, CA 94010
415/697-0440

Hamid Farzan
Senior Research Engineer
Babcock & Wilcox
1562 Beeson Street
Alliance, OH 44601
216/821-9110

Howard Feibus
Dir., Office of Coal Combustion
U.S. Department of Energy
F#-232, GTN
Washington, DC 20545
301/353-4348

W. D. Fellows
Senior Staff Engineer
Exxon Research & Engineering Co.
P.O. Box 101
Florham Park, NJ 07932
201/765-1250

P. G. Finlay
Head, Electric Power Section
Environment Canada
351 St. Joseph Blvd., 13th Floor
Ottawa, Ontario K1A 0H3
CANADA
819/953-1126

Dave Finnegan
Counsel
Committee on Energy and Commerce
2125 Rayburn Building
Washington, DC 20515
202/225-2927

Kelly A. Fortin
Environmental Engineer
U.S. EPA -- Region 9
2921 Santos Lane, Apt. 2126
Walnut Creek, CA 94596
415/974-7043

Bill Fraser
Senior Vice President
TransAlta Utilities
P.O. Box 1900
Calgary, Alberta
CANADA T2P 2M1
403/267-7482

Steve Frey
N/A
U.S. EPA -- Region 9
215 Fremont Street
San Francisco, CA 94105
415/974-8071

Yuan Fu
Chemical Engineer
U.S. Department of Energy
P.O. Box 10940
Pittsburgh, PA 15236
412/892-4841

Rajendra P. Gaikwad
Engineer
Ontario Hydro
800 Kipling Avenue
Toronto, Ontario
CANADA M5L 2Z6
416/231-4111

Michael Gamburg
Regional Sales Manager
Fuel Tech
750 17th Ave., Suite 102
San Francisco, CA 94121
415 221-6177

Gerald M. Gardetta
Environmental Affairs Admin.
Southern California Gas Company
810 S. Flower Street
Los Angeles, CA 90017
213/689-3365

James S. Geier
Public Health Engineer
Colorado Department of Health
4210 East 11th Avenue
Denver, CO 80220
303/331-8500

John Gerdes
Design Engineer
John Zink Company
P.O. Box 702220
Tulsa, OK 74170
918/592-4810

Marco Ghiringhelli
Liaison Engineer
Ansaldo -- Babcock & Wilcox
20 S. Van Buren Avenue
Barberton, OH 44203
216/860-6029

Robert L. Gilbert
Program Manager
MK-Ferguson Company
One Erieview Plaza
Cleveland, OH 44114
216/523-6618

Alan F. Gillespie
Manager, Engineering Services
Foster Wheeler, Ltd.
P.O. Box 3007
St. Catharines, Ontario
L2R 7B7, CANADA
416/688-4434

Tom P. Gilmore
Product Line Manager
KTI Corporation
1333 S. Mayflower Avenue
Monrovia, CA 91016-4099
818/303-4711

Dan V. Giovanni
Consultant
Electric Power Technologies, Inc.
P.O. Box 5560
Berkeley, Ca 94705
415 653-6422

Lisa Glatch
Process Engineer
Fluor Daniel
3333 Michelson Drive, MC-B1B
Irvine, CA 92730
714/975-3047

Frans Goudriaan
Senior Process Technologist
Kon./Shell Laboratory
Badhuisweg 3, Dept. HCP
1031 CM Amsterdam
HOLLAND
31/20 303957

Toby R. Gouker
Mgr., Stationary Emission Control
W. R. Grace & Company
7379 Route 32
Columbia, MD 21044
301/531-4131

John T. Graves
Environmental Superintendent
Minnkota Power Cooperative
P.O. Box 127
Center, ND 58530
701/794-8711

Francois Grimard
N/A
Fuel Tech Europe, Ltd.
28a Cadogan Square
London, SWIX OJH
UNITED KINGDOM
01/581-2051

Michael Grimsberg
M. Sc.
University of Lund
Dept. Chem. Engineering
P.O. Box 124
S-221 00 Lund, SWEDEN
46/46 10 82 76

Charles W. Grinnell
V.P. and General Counsel
Fuel Tech
61 Taylor Reed Place
Stamford, CT 06906
203/359-1320

Robert R. Grinstead
Associate Scientist
Dow Chemical USA
2800 Mitchell Drive
Walnut Creek, CA 94598
415/944-2077

P. A. Gristwood
Head Combustion Technology Group
Babcock Energy, Ltd.
165 Great Dover Street
London SE1 4YB
ENGLAND
01/407 8383 X2272

George Gunter
Corporate Engineering Specialist
New Brunswick Power
P.O. Box 2000
Fredericton, New Brunswick
CANADA E3B 4X1
506/458-4381

Vir V. Gupta
EPE IV
U.S. EPA
200 Churchill Road
P.O. Box 19276
Springfield, IL 62794-9276
217/782-2113

Jim Guthrie
Mechanical Engineer
California Air Resources Board
P.O. Box 2815
Sacramento, CA 95812
916/327-1508

Donald K. Hagar
President
Eagleair, Inc.
1150 Mauch Chunk Road
Bethlehem, PA 18018
215/868-1616

Leo E. Hakka
New Venture Manager
Union Carbide Canada, Ltd.
P.O. Box 700
Pointe-Aux-Trembles, Que
CANADA H1B 5KE
514/493-2617

Bob Hall
Chief, Combustion Research Branch
U.S. EPA
AEERL -- MD-65
Research Triangle Park, NC 27711
919/541-2477

David Ham
Vice President
PSI Technology Company
P.O. Box 3100
Andover, MA 01810
508/475-9030

Richard Haman
Principal Engineer
Detroit Edison
2000 Second Avenue
Detroit, MI 48226
313/897-0208

Peter J. Handy
Engineering Sales Director
Rolls Royce Canada
P.O. Box 544, Montreal AMF
Montreal, Quebec
CANADA H4Y 1B3
514/631-3541

Thomas Hansen
Chief, Mobile Source Section
U.S. EPA
345 Courtland Street
Atlanta, GA 30365
404/347-2864

Stan Harding
Research Group Leader
Consolidation Coal Company
4000 Brownsville Road
Library, PA 15129
412/854-6735

Peter J. Hart
Supervisor, Emissions Comp.
Allison Gas Turbine Div. of GM
P.O. Box 420, SC T-01
Indianapolis, IN 46206
317 230-4186

Scott Hassett
Principal Engineer
Utah Power & Light Company
168 North, 1950 West
Salt Lake City, UT 84140
801/220-4839

Greg Haussmann
Research Assistant
Stanford School of Engineering
Blgd. 520, Dept. of Mech. Engrng.
Stanford, CA 94305
415/723-1823

Edward Healy
Project Planning Engineer
Southern Company Services
P.O. Box 2625
Birmingham, AL 35202
205/868-5212

Dietmar Hein
Professor
Siemens AG, KWU Group
Hammerbacherstrasse 12+14
D-8520 Erlangen
FEDERAL REPUBLIC OF GERMANY
9131/182350

Klaus Hein
Prof. Dr-Ing.
RWE AG, BV Fortuna
Postfach 1461
5010 Bergheim 4
FEDERAL REPUBLIC OF GERMANY
02271/584-2234

Todd Hellewell
Principal Engineer
Combustion Engineering
1000 Prospect Hill Road
Windsor, CT 06095
203/285-4919

Eric Hennen
Environmental Engineer
Dairyland Power Company
2615 East Avenue, So.
Lacrosse, WI 54601
608/787-1371

Bo Herrlander
Business Area Manager
Flakt Industres AB
S-35187 Vaxjo
SWEDEN
01146/470-87400

Steven A. Hickerson
President
Emcotek Corporation
8220 Doe Avenue
Visalia, CA 93291
209/651-2000

David Hickman
Senior Scientist
Corning Glass Works
SP-FR-6-1
Corning, NY 14831
607/974-3715

M. B. Hilt
Mgr., Externally Funded Programs
General Electric
1 River Road
Schenectady, NY 12345
518/385-9191

Anna Hinderson
Engineer
ABB Carbon
Box S61220
SWEDEN
N/A

Anna-Karin E. Hjalmarsson
Environment Group
IEA Coal Research
14-15 Lower Grosvenor Place
London SW1W 0EX ENGLAND
01/828-4661

Lennart Hjalmarsson
Engineer
ABB Carbon
Box S61220
SWEDEN
N/A

Patrick A. Ho
Principal Engineer
Tampa Electric Company
702 N. Franklin Street
Tampa, FL 33602
813/228-4844

John E. Hofmann
Vice President, Development
Fuel Tech
61 Taylor Reed Place
Stamford, CT 06906
203/359-1320

Bill Holt
Manager, Business Development
Allied Signal
P.O. Box 580970
Tulsa, OK 74158-0970
918/266-1400

Neville Holt
Senior Program Manager
Electric Power Research Institute
3412 Hillview Avenue
Palo Alto, Ca 94034
415/855-2503

Richard G. Hooper
Vice President
NaTec, Ltd.
216 Sixteenth Street Mall
Suite 1500
Denver, CO 80202-5129
303/820-5200

Hann S. Huang
Chemical Engineer
Argonne National Laboratory
9700 S. Cass Avenue
Argonne, IL 60439
312/972-3125

Allen Hubbard
Environmental Engineer
Wis. Dept. of Natural Resources
P.O. Box 7921
Madison, WI 53707
608/266-3450

Terry Hunt
Mechanical Engineer
Public Service Co. of Colorado
5900 East 39th Avenue
Denver, CO 80207
303/329-1113

Adrian Hyde
Engineer
UK Department of Energy
Thames House South, Millbank
London, SW11 4QT
UNITED KINGDOM
01/211-4547

Ivan V. Insua
Staff Engineer
Salt River Project
P.O. Box 52025
Phoenix, AZ 85072-2025
608/236-5240

Paul Ireland
Project Engineering Manager
United Engineers & Constructors
P.O. Box 5888
Denver, CO 80217
303/692-3420

Reda S. Iskandar
Project Manager
Corning Glass Works
MP-WX-01-5
Corning, NY 14831
607/974-7306

Sven Jaras
Engineer
Eka Novel AB
S-445 01 Surte
SWEDEN
+46/303 98377

Jim Jarvis
Senior Engineer
Radian Corporation
8501 Mo-Pac
Austin, TX 78720
512/454-4797

Torgny Johansson
Manager Process Technology
Flakt Industres AB
S-35187 Vaxso
SWEDEN
01146 470-8700 0

David L. Johnson
Mgr., Production, Engrng, & Const.
Otter Tail Power Company
215 S. Cascade Street
Fergus Falls, MN 56537
218/739-8399

Keith Johnson
N/A
Foster Wheeler Power Products
Olympic Office Center
No. 8 Fulton Road
Wembly, Middlesex HA9 OJH, UK
01/900-2533

Kevin L. Johnson
Project Manager
Radian Corporation
3200 E. Chapel Hill Road
Research Triangle Park, NC 27709
919/541-9100

Steve Johnson
Mgr., Applied Combustion Tech.
PSI Technology Company
P.O. Box 3100
Andover, MA 01810
508/475-9030

Wayne L. Johnson
Sr. Process Engineering Specialist
ESSO Resources Canada, Ltd.
237 Fourth Avenue, S.W.
Calgary, Alberta
CANADA T2P 0N6
403/237-2721

Dale G. Jones
Vice President
Emcotek Corporation
8220 Doe Avenue
Visalia, CA 92391
209/651-2000

Gary D. Jones
Program Manager
Radian Corporation
P.O. Box 13000
Research Triangle Park, NC 27709
919 541-9100

Thomas E. Kaforey
Generating Plant Engineer
Ohio Edison Company
76 South Main Street
Akron, OH 44308
216/384-5974

Marie Kalinowski
Advanced Scientist
Owens Corning Fiberglas
Route 16
Granville, OH 43023
614/587-7620

Dale A. Kanary
Engineer
Ohio Edison Company
76 South Main Street
Akron, OH 44308
216/384-5744

Hans T. Karlsson
Associate Professor
University of Lund
Dept. Chem. Engineering Box 124
S-221 00 Lund, SWEDEN
46 46 10 82 44

Ari Karppinen
Research Scientist
Finnish Meteorological Institute
Sahaajankatu 22E
SF 00810 Helsinki
FINLAND
358/0 7581345

Robert F. Kaupp
Marketing Manager, Projects
Johnson Matthey
436 Devon Park Drive
Wayne, PA 19087
215/341-8502

Martin Kay
Supervising Air Quality Engineer
So. Coast Air Quality Mgmnt. Dist.
9150 Flair Drive
El Monte, CA 91731
818/572-6258

Robert T. Keen
Principal Engineer
Fichtner USA, Inc.
Overlook 1, Suite 360
2849 Paces Ferry Road, N.W.
Atlanta, GA 30339
404/432-6983

Robert L. Keller
Corporate Engineer
Dayton Power & Light Company
9200 Chautauqua Road
Miamisburgh, OH 45342
513/865-6234

Stephen E. Kerho
Consultant
Electric Power Technologies, Inc.
25108 Marguerite Pkwy., Ste 8239
Mission Viejo, CA 92692
714 380-7316

Fred Kessler
Project Manager
KTI Corporation
1333 S. Mayflower Avenue
Monrovia, CA 91016
818/303-4711

Lawrence P. King
Senior Marketing Specialist
Babcock & Wilcox
1562 Beeson Street
Alliance, OH 44601
216/829-7576

Masaaki Kinoshita
Assistant Manager
Mitsubishi Heavy Industries
1-1, Akunoura-Machi
Nagasaki, JAPAN
0958/28-6431

Larry H. Kirby
Assoc. Development Scientist
Dow Chemical USA
Texas Operations, B-1605 Building
Freeport, TX 77541
409/238-7721

Thomas Kirkey
Account Manager
Norton Company
2500 E. Ball Road
Anaheim, CA 92806
714/635-4051

John B. Kitto, Jr.
Program Manager
Babcock & Wilcox
Research & Development Division
1562 Beeson Street
Alliance, OH 44601
216/829-7710

J. S. Klingspor
Senior Engineer
Combustion Engineering
31 Inverness Center Parkway
Birmingham, AL 35243
205/991-2832

Jeff Klueger
Associate Mechanical Engineer
Los Angeles Dept. of Water & Power
111 N. Hope Street, Room 661
Los Angeles, CA 90051
213/481-4647

Kevin Knill
Research Engineer
Int'l Flame Research Foundation
P.O. Box 10000
1970 CA Ijmuiden
THE NETHERLANDS
31/2510-9364

Cathy L. Knowles
Fibers Department
E.I. du Pont de Nemours & Co., Inc.
Laurel Run Building
P.O. Box 80, 705
Wilmington, DE 19880-0705
302/999-3905

Kris W. Knudsen
Supervising Scientist
Duke Power Company
P.O. Box 33189
Charlotte, NC 28242
704/373-5104

Bernie Koch
Director, Project Development
Consolidation Coal Company
4000 Brownsville Road
Library, PA 15129
412/854-6612

A. Kok
Engineer
NOVEM
P.O. Box 17
6130 AA Sittard
THE NETHERLANDS
4490/95308

Angelos Kokkinos
Project Manager
Electric Power Research Institute
3412 Hillview Avenue
Palo Alto, CA 94304
415/855-2494

Johanna Koppius-Odink
Engineer
EPON
P.O. Box 10087
8000 GB Zwolle
THE NETHERLANDS
038/272900

Richard S. Kostkas
Dir., Special Marketing Projects
The Peoples Natural Gas Company
625 Liberty Avenue
Pittsburgh, PA 15222
412/553-6608

Toshio Koyanagi
SCR Engineer
Mitsubishi Heavy Industry
2 Houston Center
Houston, TX 77010
713/652-9269

Donald E. Krider
Mgr., Thermal De-NOx Sales
Exxon Research & Engineering Co.
P.O. Box 390
Florham Park, NJ 07932
201/765-2339

Hal M. Kruger
Engineer
Centerior Energy
P.O. Box 94661
Cleveland, OH 44101-4661
216/447-2233

H. Kulper
Manager, Fuel & Burner Department
Royal Schelde
P.O. Box 16, 4380AA
Vlissingen, NETHERLANDS
311184 82583

Robin L. Kump
Environmental Consultant
E. I. DuPont
P.O. Box 1089
Orange, TX 77631-1089
409/886-6239

Alfred Kurzenhauser
Technical Support Supervisor
LFC Power Systems Corporation
Building One, Suite 255
4000 Kruse Way Place
Lake Oswego, OR 97035
503/697-0259

H. K. Kwee
Engineer
Stork Boilers B.V.
P.O. Box 20
7550 GB Hengelo
THE NETHERLANDS
31/74 401857

D. C. Langley
Regional Service Manager
Babcock & Wilcox
7401 W. Mansfield Avenue, #410
Lakewood, CO 80235
303/988-8203

Robert Langthorne
Manager
Canadian Energy Services, Ltd.
401 Salter Street
New Westminster, B.C.
CANADA V3M 5Y1
604/521-3322

Dorothy Lau
Design Specialist
Ontario Hydro
700 University Avenue, H10 F2
Toronto, Ontario M5G 1X6
CANADA
416/592-7306

Dennis Laudal
Research Engineer
Energy & Mineral Research Center
15 North 23rd Street
P.O. Box 8213
Grand Forks, ND 58201-8213
701/777-5138

Nick J. Lavingia
Senior Project Engineer
Chevron U.S.A.
324 W. El Segundo Boulevard
El Segundo, CA 90245
213/615-5784

Peter Lawson
Supervising Engineer
Ontario Hydro
700 University Avenue
Toronto, Ontario
CANADA M5G 1X6
416/592-5393

Albert D. LaRue
Principal Engineer
Babcock & Wilcox
20 S. Van Buren Avenue
Barberton, OH
216/860-1493

Douglas J. Leadenham
Analyst
Electric Power Research Institute
3412 Hillview Avenue
Palo Alto, CA 94304
415/855-2954

G. K. Lee
Manager, Combustion Research
Energy Resources Canada
555 Booth Street
Ottawa, Ontario K2G 0N3
613/996-3179

George C. Lee
Engineering Specialist
Bechtel National, Inc.
50 Beale Street
San Francisco, CA 94105
415/768-1216

Yam Y. Lee
Research Specialist
Pyropower Corporation
5120 Shoreham Place
San Diego, CA 92122
619/552-2312

George R. Lester
Senior Research Scientist
Allied Signal
P.O. Box 5016
Des Plaines, IL 60017
312/391-3314

Robert D. Lewis
Principal Engineer
Combustion Engineering
1000 Prospect Hill Road
Windsor, CT 06095
203/285-5968

F. Y. Liao
Senior Associate Engineer
Mobil R&D
P.O. Box 1026
Princeton, NJ 08540
609/737-4955

Vladimir Lifshits
N/A
Coen Company
1510 Rollins Road
Burlingame, CA 94010
415/697-0440

Sergio Ligasacchi
N/A
ENEL
Via A. Pisano 120
Pisa, ITALY 56100
050/535622

JoAnn S. Lighty
Assistant Professor
University of Utah
2254 MEB
Salt Lake City, UT 84112
801/581-5763

William P. Linak
Project Officer
U.S. EPA
AEERL -- MD-65
Research Triangle Park, NC 27711
919/541-5792

David G. Linz
Mgr., Land and Water Quality Res.
Gas Research Institute
8600 West Bryn Mawr Avenue
Chicago, IL 60631
312/399-8198

Robert A. Lisauskas
Director, Research & Development
Riley Stoker Corporation
Riley Research Center
45 McKeon Road
Worcester, MA 01610
508/792-4801

Steve Londerville
N/A
Coen Company
1510 Rollins Road
Burlingame, CA 94010
415/697-0440

Phillip A. Lowe
President
Intech, Inc.
11316 Roven Drive
Potomac, MD 20054
301/983-9367

Francis C. Luck
Research Engineer
Rhone-Poulenc France
14 Rue des Gardinoux
93308 Aubervilliers, FRANCE
33/147-396-361

Richard K. Lyon
Senior Scientist
Energy & Environmental Research
P.O. Box 189
Whitehouse, NJ 08888
201/534-5833

O. L. Maaskant
N/A
Shell International Chemical Co.
P.O. Box 162
2501 AN The Hague
HOLLAND
070/773741

Denis Maftei
Sr. Process Engineer
Environment Ontario
880 Bay Street, 4th Floor
Toronto, Ontario
CANADA M5S 1Z8
416/965-5776

Mehdi Maibodi
Engineer
Radian Corporation
P.O. Box 13000
Research Triangle Park, NC 27709
919/541-9100

Jason Makansi
Senior Technical Editor
Power Magazine
11 W. 19th Street, 2nd Floor
New York, NY 10011
212/337-4074

James W. Malone
Sales Engineer
Babcock & Wilcox
3734 Gundry Avenue
Long Beach, CA 90807
213/595-8357

Aaron Mann
N/A
Sierra Pacific Power Company
P.O. Box 10100
Reno, NV 89520
702/689-4011

M. N. Mansour
President
Applied Utility Systems
1140 E. Chestnut Avenue
Santa Ana, CA 92701
714/953-9922

Gerald J. Maringo
Development Engineer
Babcock & Wilcox
20 S. Van Buren Avenue
Barberton, OH 44203
216/860-6321

John L. Marion
Consulting Engineer
Combustion Engineering
1000 Prospect Hill Road
Windsor, CT 06095
203/285-4539

Bob Markoja
Manager, Environmental Services
Sierra Environmental Engineering
3505 Cadillac Avenue, N-3
Costa Mesa, CA 92626
714/432-0330

Gregory A. Martel
Senior Engineer
Northeast Utilities
1866 River Road
Middletown, CT 06457
203/638-3175

Blair Martin
Deputy Director, AEERL
U.S. EPA
AEERL -- MD-60
Research Triangle Park, NC 27711
919/541-7504

Gianni Mascalze
Doctor
Ansaldo Componenti Spa
V.Le Sarca 336
Milano, ITALY 20126
2/6445 2570

Howard Mason
Mgr., Energy Engineering Department
Acurex Corporation
485 Clyde Avenue
Mountain View, CA 94039
415/961-5700

M. Massoudi
Project Manager
Ebasco Services, Inc.
One Parket Plaza, Spear Bldg.
Suite 600
San Francisco, CA 94105
415/777-3000

Mike Maxwell
Chief, Technology Dev. Branch
U.S. EPA
AEERL -- MD-04
Research Triangle Park, NC 27711
919/541-3091

Phil May
Project Director
Radian Corporation
P.O. Box 13000
Research Triangle Park, NC 27709
919/541-9100

Michael McCartney
Mgr., Firing Systems Engineering
Combustion Engineering
1000 Prospect Hill Road
Windsor, CT 06095
203/285-4677

Michael W. McElroy
Consultant
Electric Power Technologies, Inc.
P.O. Box 307
Menlo Park, CA 94026
415 322-0843

Marilyn McIlvane
Managing Editor
McIlvane Company
2970 Maria Avenue
Northbrook, IL 60062
312/272-0010

Robert McIlvaine
President
McIlvane Company
2970 Maria Avenue
Northbrook, IL 60062
312/272-0010

William M. McKinney
V.P., New Business Development
United Catalysts, Inc.
P.O. Box 32370
Louisville, KY 40232
502/634-7218

Ron Melton
Section Manager
Battelle Northwest
P.O. Box 999
Richland, WA 99352
509/375-2932

Jim Merriam
Sr. Environmental Licensing Engr.
Jersey Central Power & Light Co.
310 Madison Avenue
Morristown, NJ 07960
201/455-8563

Jean Mevel
Test Manager, Research & Dev.
Stein Industries
1921 Morane Saulnier Avenue
Velizy, Vellacoublay
FRANCE
1/34 65 44 48

James E. Meyers
Chemical Equipment Engineer
Detroit Edison
2000 Second Avenue
Detroit, MI 48226
313/897-0806

Paul G. Mikolaj
Consulting Engineer
Tosco Corporation
Avon Refinery
Martinez, CA 94553
415/228-1880

Thomas Mileus
Sales Manager
Flakt Industres AB
S-351 87 Vaxjo
SWEDEN
01146 470-87000

Scott A. Miller
Staff Engineer
Dayton Power & Light Company
P.O. Box 468
Aberdeen, OH 45101
513/549-2641 X5127

Kenneth J. Mills
Market Manager
Norton Company
P.O. Box 350
Akron, OH 44309
216/673-5860

Ed Milone
Engineer
Con. Edison Co. of New York
4 Irving Place
New York, NY 10003
212/460-4887

Shigehiro Miyamae
Senior Engineer
Ishikawajima-Harima Heavy Ind.
2-16, Toyosu 3-chome, Koto-ku
Tokyo 135 JAPAN
03/534-4335

Cal Mock
District Manager
Babcock & Wilcox
1990 N. California Boulevard
Walnut Creek, CA 94596
415/947-1100

Hukam C. Mongia
Chief, Combustors R&D
Allison Gas Turbine Div. of GM
P.O. Box 420, Speed Code T14
Indianapolis, IN 46206-0420
317 230-5945

Curtis A. Moore
Counsel
U.S. Senate
Washington, DC 20510
202/224-5762

Dave Moore
Supervisor
Dayton Power & Light Company
Killen Station -- P.O. Box 147
Manchester, OH 45144
513/549-3911

K. A. Moore
N/A
Dykema Engineering
5850 Canoga Avenue, Suite 400
Woodland Hills, CA 91367
818/712-0070

Tom Morasky
Tech. Transfer Manager
Electric Power Research Institute
3412 Hillview Avenue
Palo Alto, CA 94034
415/855-2468

Akira Mori
Senior Engineer
Hitachi, Ltd.
c/o Hitachi America. Ltd.
950 Elm Avenue, Suite 195
San Bruno, CA 94066-3094
415/872-1902 X8131

Shigeki Morita
Senior Engineer, Kure Works
Babcock-Hitachi K. K.
c/o Hitachi America, Ltd.
950 Elm Avenue, Suite 195
San Bruno, CA 94066-3094
415/872-1902 X8131

Karen D. Morris
Mechanical Engineer
Pacific Gas & Electric
77 Beale Street, Room 2547
San Francisco, CA 94106
415 972-3384

J. K. Mueller
Project Manager
Unocal Corporation
1201 West 5th Street
Los Angeles, CA 90051
213/977-6419

T. Murataka
Senior Engineer
Babcock-Hitachi K. K.
c/o Hitachi America, Ltd.
950 Elm Avenue, Suite 195
San Bruno, CA 94066-3094
415/872-1902

Hitoshi Murayama
Project Manager
Electric Power Research Institute
3412 Hillview Avenue
Palo Alto, CA 94304
415/855-2777

Paul Musser
Program Manager
U.S. Department of Energy
Germantown, MD 20874
301/353-2846

Lawrence J. Muzio
Vice President
Fossil Energy Research Corporation
23342 C South Pointe
Laguna Hills, CA 92653
714/859-4466

Peter Necker
Prokurist
Neckarwerke AG
Kuferstrasse 2
7300 Esslingen am Neckar
FEDERAL REPUBLIC OF GERMANY
0711/3190-3001

Stefan Negrea
N/A
KRC/Noell GnbH
Alfred, Nobel Strasse 20
D-8700 Wurgburg
WEST GERMANY
N/A

Mike Nelson
Senior Engineer
Southern Company Services
P.O. Box 2625
Birmingham, AL 35202
205/870-6518

Kenneth M. Nichols
Asst. Prof., Engineering & Research
The Institute of Paper Chemistry
P.O. Box 1039
Appleton, WI 54912
414/738-3385

Per R. Nielsen
Senior Manager
Nordic Gas Technology Center
Dr. Neergaardsvej 5A
DK 2970 Hoersholm
DENMARK
45/276 6995

Ralph M. Nigro
Project Engineer
Delmarva Power
800 King Street
Wilmington, DE 19899
302/454-4872

Michael Novak
Engineer
Verbundkraft Elek.
AM HOF 6 A
Vienna A-1011 Wein
AUSTRIA
222/531 13 2590

James H. Nylander
Senior Engineer
San Diego Gas & Electric Co.
P.O. Box 1831
San Diego, CA 92112
619/931-7294

George Offen
Program Manager
Electric Power Research Institute
3412 Hillview Avenue
Palo Alto, CA 94304
415/855-8942

Yoshiya Ogasawara
Asst. Manager, Int'l Sales Div.
Hitachi, Ltd.
c/o Hitachi America, Ltd.
950 Elm Avenue, Suite 195
San Bruno, CA 94066-3094
415/872-1902 X8131

Delbert M. Ottmers, Jr.
Vice President
Radian Corporation
P.O. Box 201088
Austin, TX 78720-1088
512/454-4797

Joseph H. Oxley
Program Manager
Battelle
505 King Avenue
Columbus, OH 43201-2693
614/424-7885

Y. S. Pan
Project Coordinator
U.S. Department of Energy
P.O. Box 10940
Pittsburgh, PA 15236
412/892-5727

Andy S. Paranjape
Senior Project Engineer
Kerr-McGee Corporation
P.O. Box 25861
Oklahoma City, OK 73125
405/270-2906

Rasik Patel
Manager, Thermal Design
KTI Corporation
1333 S. Mayflower Avenue
Monrovia, CA 91016-4099
818/303-4711

Jarl Pedersen
Mgr., Combustion Systems
Burmeister & Wain Energy
23 Teknikerbyen
Virum, DENMARK, 2830
45/285-2100

Craig Penterson
Staff Engineer, R&D
Riley Stoker Corporation
5 Neponset Street
Worcester, MA 01590
508/792-4829

Ralph Perhac
Department Director
Electric Power Research Institute
3412 Hillview Avenue
Palo Alto, CA 94304
415/855-2572

Michael Perlsweig
Flue Gas Cleanup Program Manager
U.S. Department of Energy
Fossil Energy, FE-23
Washington, DC 20545
301/353-4399

David W. Pershing
Dean, College of Engineering
University of Utah
2202 MEB
Salt Lake City, UT 84112
801/581-5057

Robert D. Petersen
Senior Mechanical Engineer
Burns & McDonnell
4800 East 63rd Street
Kansas City, MO 64141
816/333-4375

Ellen Petrill
Project Manager
Electric Power Research Institute
3412 Hillview Avenue
Palo Alto, CA 94304
415/855-8989

James D. Phillip
Plant Chemist
Tenneco Minerals Company
P.O. Box 1167
Green River, WY 82935
307/872-6519

Larry A. Pierson
Project Manager
Babcock & Wilcox
20 S. Van Buren Avenue
Barberton, OH 44203
216/860-1103

Everett L. Plyler
Dir., Combustion & Indoor Air Div.
U.S. EPA
AEERL -- MD-54
Research Triangle Park, NC 27711
919/541-2918

Gary Poe
Project Manager
Electric Power Research Institute
3412 Hillview Avenue
Palo Alto, CA 94304
415/855-8969

John H. Pohl
Dir., Research & Development
Energy Systems Associates
15991 Red Hill
Tustin, CA 92680
714/259-9520

David Price
Project Engineer
Unocal Corporation
P.O. Box 758
Wilmington, CA 90748
213/513-7600

W. L. Prins
Manager, Process Technology
Tests Engineers & Consultants
P.O. Box 10.000
1970 CA Ijmuiden
THE NETHERLANDS
+312510 98603/92209

Walter Puille
Technology Transfer Manager
Electric Power Research Institute
3412 Hillview Avenue
Palo Alto, CA 94304
415/855-2470

Suresh K. Punatar
Engineering Supervisor
Bechtel Power Corporation
50 Beale Street
San Francisco, CA 94119
415/768-0495

Brian Quil
Mechanical Engineer
Naval Energy & Environmental Suppt.
NEESA 11A
Port Hueneme, CA 93043
805/982-4748

Les Radak
Senior Research Engineer
Southern California Edison
2244 Walnut Grove Avenue
Rosemead, CA 91770
818/302-9746

Paul Radcliffe
Project Manager
Electric Power Research Institute
3412 Hillview Avenue
Palo Alto, CA 94304
415/855-2720

James M. Rames
Sr. Mechanical Engineer
Pacific Gas & Electric
77 Beale Street, Room 2553
San Francisco, CA 94106
415 972-2735

Jay Ratafia-Brown
Dir., Fossil Energy/Env. Projects
SAIC
1710 Goodridge Drive
P.O. Box 1303
McLean, VA 22102
703/448-6343

James L. Reese
Consulting Engineer
Applied Utility Systems
1140 E. Chestnut Avenue
Santa Ana, CA 92701
714/953-9922

Joseph N. Reeves
Research Manager
Southern California Edison
2244 Walnut Grove Avenue
Rosemead, CA 91770
818/302-9515

Amir Rehmat
Mgr., Utility Gas Development
Institute of Gas Technology
3424 South State Street
Chicago, IL 60616-3896
312/567-5899

Ernst Ringle
Delegate
Noell
199 Wells Avenue
Newton, MA 02159
617/332-6510

Alan P. Risch
Manager, Technical Marketing
UOP
39 Old Ridgebury Road
Danbury, CT 06817
208/794-5542

R. C. Rittenhouse
Senior Editor
Power Engineering Magazine
1250 S. Grove Avenue, Suite 302
Barrington, IL 60010
312/382-2450

Roger Robb
Senior Engineer
Northern Indiana Public Service Co.
5265 Hohman Avenue
Hammond, IN 46320
219/853-5821

Dick Robertson
Manager, Air Quality
TU Electric
400 North Olive, LB-81
Dallas, TX 75201
214/812-8416

Chris P. Robie
Process Engineer
United Engineers & Constructors
700 South Ash Street
P.O. Box 5888
Denver, CO 80217
303/692-2803

Tracy M. Robinson
Marketing Programs Manager
Fuel Tech
61 Taylor Reed Place
Stamford, CT 06906
203/359-1320

William Rogers
Sales Engineer
Engelhard Corporation
2000 Powell Street
Emeryville, CA 94608
415/596-1703

Bill Rovesti
Senior Project Manager
Electric Power Research Institute
3412 Hillview Avenue
Palo Alto, CA 94304
415/855-2519

Charlie Rowden
Lead Process Engineer
Fluor Daniel
3333 Michelson Drive
Irvine, CA 92730
714/975-3047

Richard E. Rozelle
Project Manager
Dow Chemical USA
Texas Operations, B-1605 Bldg.
Freeport, TX 77541
409/238-9846

Hans-Georg Rych
Electric Power Systems Division
EVN
Johann-Steinbock-Strasse 1
A-2344 Maria Enzersdorf am Gebirge
AUSTRIA
02236/83 611 526

N. C. Samish
Staff Research Engineer
Shell Development Company
P.O. Box 1380
Houston, TX 77251
713/493-7944

Henry Sanematsu
Mechanical Engineer
Los Angeles Dept. of Water & Power
111 N. Hope Street
Los Angeles, CA 90012
213/481-4906

Charles E. Schlittler
Program Manager
Kerr-McGee Corporation
P.O. Box 25861
Oklahoma City, OK 73125
405/270-3188

Herbert Schuster
Head, Combustion R&D Dept.
Deutsche Babcock Werke AG
Duisburger Str. 375
D-4200 Oberhausen 1
FEDERAL REPUBLIC OF GERMANY
0208/833-2853

Charlie Sedman
Project Officer
U.S. EPA
AEERL -- MD-62
Research Triangle Park, NC 27711
919/541-7700

Noriyuki Shimizu
Assistant Manager
Electric Power Development Co.
15-1, Ginza, 6-chome, Chuo-ku
Tokyo, JAPAN 104
3/546-9403

Gary H. Shiomoto
Engineer
Fossil Energy Research Corporation
23342 C South Pointe
Laguna Hills, CA 92653
714/859-4466

Dale E. Shore
Manager, Western Region
Energy Systems Associates
15991 Red Hill Avenue, Suite 110
Tustin, CA 92680
714/259-9520

Stefan P. Shoup
Senior Staff Engineer
Inland Steel Company
3210 Watling Street
East Chicago, IL 46312
219/399-5733

George Shulof
President & CEO
Fuel Tech
61 Taylor Reed Place
Stamford, CT 06906
203/359-1320

Sandy Simko
Project Manager
Radian Corporation
P.O. Box 201088
Austin, TX 78720-1088
512/454-4797 X5301

Robert E. Sistek
Environmental Met. Engineer
LTV Steel Company
3100 E. 45th Street
Cleveland, OH 44127
216/429-6477

Lowell L. Smith
Vice President
ETEC
2091 Business Center Drive #100
Irvine, CA 92715
714/833-2523

Richard C. Smith
Supervising Engineer
Union Electric Company
P.O. Box 149, MC-450
St. Louis, MO 63166
314/554-3529

Douglas Smoot
Dean, College of Engrng. & Tech.
Brigham Young University
270 Clyde Building
Provo, UT 84602
801/378-4327

Gerry C. Snow
Senior Engineer
Radian Corporation
P.O. Box 13000
Research Triangle Park, NC 27709
919/541-9100

David W. South
Economist
Argonne National Laboratory
370 L'Enfant Promenade, S.W.
Suite 702
Washington, DC 20024
202/586-4758

Ruggero Spagliarisi
Engineer
Aeru -- Milano
Via S. Sisto
8-20123
Milano, ITALY
02/808966

Barry Speronello
Principal Scientist
Engelhard Corporation
Menlo Park
Edison, NJ 08818
201/321-5155

Dan Spisak
Project Engineer
Bechtel National, Inc.
50 Beale Street
San Francisco, CA 94105
415/768-1645

Richard T. Squires
Research Officer
CEGB
Marchwood Labs
Marchwood, Southampton
UNITED KINGDOM
0703/663232

Ravi K. Srivastava
Project Engineer
Acurex Corporation
P.O. Box 13109
Research Triangle Park, NC 27709
919/541-2692

Susan J. Stamey
Mechanical Engineer
Tennessee Valley Authority
MR3S92B
Chattanooga, TN 37402
615/751-5324

Mark T. Staniulis
Senior Staff Chemist
UOP
Old Sawmill River Road
Tarrytown, NY 10591
914/789-3865

David L. Stavenger
N/A
Dow Chemical USA
2020 Willard H. Dow Center
Midland, MI 48674
517/636-5236

Harry Stecyk
Sr. Engineering Specialist
ESSO Resources Canada, Ltd.
237 Fourth Avenue, S.W.
Calgary, Alberta
CANADA T2P 0H6
403/237-2721

Harvey Stenger
Professor
Lehigh University
Building A, MTC
Dept. of Chemical Engrng.
Bethlehem, PA 18015
215/758-4791

Donald J. Stepson
Marketing Director
Rolls-Royce, Inc.
16800 Greenspoint Park Drive
Suite 155S
Houston, TX 77060
713/875-2100

Dick D. Stern
Chief, Technology Applications Br.
U.S. EPA
AEERL -- MD-63
Research Triangle Park, NC 27711
919/541-2973

Jim E. Stresewski
Engineer
Black & Veatch
1500 Meadow Lake Parkway
Kansas City, MO 64114
913/339-2000

Y. P. Su
Principal Environmental Engineer
Stone & Webster Engineering Corp.
330 Barker Cypress
Houston, TX 77094
713/492-4334

Keith Summons
Senior Design Specialist
Ontario Hydro
700 University Avenue, H13 C10
Toronto, Ontario
CANADA M5G 1X6
416/592-5935

Kohei Suyama
Manager
Mitsubishi Heavy Ind. America
c/o Combustion Engineering
1000 Prospect Hill Road
Windsor, CT 06095
203/285-2491

Markus Tahtinen
Research Scientist
Technical Research Ctr. of Finland
P.O. Box 169
SF-00181 Helsinki
FINLAND
358/0 648931

Katherine M. Tait
Engineer
MONENCO
400 Monenco Place, 801-6th Ave. SW
Calgary/Alta
CANADA T3C 1N1
403/298-4161

Yojiro Takahashi
Manager
Nippon Shokubai America, Inc.
101 East 52nd Street, 14th Floor
New York, NY 10022
212/759-7890

Harry S. Tang
Senior Research Engineer
Shell Development Company
P.O. Box 1380
Houston, TX 77251-1380
713/493-8424

Donald P. Teixeira
Technical Manager Fossil R&D
Pacific Gas & Electric
3400 Crow Canyon Road
San Ramon, CA 94583
415/866-5531

Robert Telesz
Marketing Manager
Babcock & Wilcox
20 S. Van Buren Avenue
Barberton, OH 44230
216/860-1103

Preston E. Tempero
Plant Manager
KPL Gas Service
Lawrence Energy Center
P.O. Box 249
Lawrence, KS 66044
913/843-8118

Jean Thomas Rose
Engineering Manager
Betz Industrial
Somerton Road
Trevose, PA 19047
215/355-3300 X2365

T. R. Thomas
N/A
Westinghouse Idaho Nuclear Company
P.O. Box 4000
Idaho Falls, ID 83403
208/526-3086

Bruce Thompson
District Manager
Nalco Chemical Company
4310 North 75th Street, Suite A
Scottsdale, AZ 85251
602/996-2238

Paul F. Thompson
President
Tenerex Corporation
303 Laurel
Friendswood, TX 77546
713/482-5801

Richard E. Thompson
President
Fossil Energy Research Corporation
23342 C South Pointe
Laguna Hills, CA 92653
714/859-4466

Richard S. Topor
Int'l Regional Manager, Licensing
Combustion Engineering
1000 Prospect Hill Road, 7110-1923
Windsor, CT 06095
203/285-9934

Majed A. Toqan
Program Manager, CRF
Massachusetts Inst. of Technology
60 Vassar Street, Bldg. 31-261
Cambridge, MA 02139
617/253-1721

Paul J. Torpey
Executive Director
Empire State Elec. Energy Res. Corp
1155 Avenue of the Americas
New York, NY 10036
212/302-1212

Ian Torrens
Department Director
Electric Power Research Institute
3412 Hillview Avenue
Palo Alto, CA 94304
415/855-2422

Sanh V. Tram
Senior Service Engineer
Babcock & Wilcox
12552 Tours Avenue
Garden Grove, CA
714/554-3844

Jay R. Turner
Research Assistant
Washington University
Chemical Engineering Department
Campus Box 1198, One Brookings Dr.
St. Louis, MO 63130
314-889-6042

James M. Valentine
V.P. Marketing & Business Dev.
Fuel Tech
61 Taylor Reed Place
Stamford, CT 06906
203/359-1320

Don Van Buren
Field Engineering
Bay Area Air Quality Mgmnt. Dist.
939 Ellis Street
San Francisco, CA 94109
415/771-6000 X165

Simon Vanderheijden
Chief Chemist
Saskatchewan Power
2025 Victoria Avenue
Regina, Saskatchewan
CANADA S4P 0S1
306/566-3073

Galliano Variali
Professor
University of Rome, Italy
Via Eudossiana 18
Rome, ITALY 00184
396/4687321

Joel Vatsky
Dir., Combustion & Env. Systems
Foster Wheeler Energy Corporation
Perryville Corporate Park
Clinton, NJ 08809-4000
201/730-5450

Gary R. Veerkamp
Sr. Mechanical Engineer
Pacific Gas & Electric
77 Beale Street, Room 2555
San Francisco, CA 94106
415/972-1576

Jan L. Vernon
Head, Environment Group
IEA Coal Research
14-15 Lower Grosvenor Place
London SW1W 0EX ENGLAND
01/828-4661

John Verurink
Senior Combustion Engineer
Stork Boilers B.V.
P.O. Box 20
7550 BD, Hengelo
THE NETHERLANDS
074/401370

Denise M. Viola
Sales Manager
Engelhard Corporation
Menlo Park CN28
Edison, NJ 08818
201/321-5039

J. Von Bergmann
General Manager
Fuel Tech GmbH
Frankfurter Strasse 33-35
Eschborn 6236
FEDERAL REPUBLIC OF GERMANY
49/6196-48613

Paul Wagner
Project Engineer
Delmarva Power
I-95 & Route 273
P.O. Box 9239
Newark, DE 19714
302/454-4844

Ali A. Wali
Planning Analyst
Wisconsin Public Service Comm.
4802 Sheboygan Avenue
P.O. Box 7854
Madison, WI 53707
608/267-3595

Mats A. Wallin
M. Sc.
University of Lund
Dept. Chem. Engineering Box 124
S-221 00 Lund, SWEDEN
46 46-108244

Ed Warchol
Engineering Specialist
ESSO Resources Canada, Ltd.
237 Fourth Avenue, S.W.
Calgary, Alberta
CANADA T2P 0N6
403/237-2721

Wendell Warnacut
Mech. Engineer
Tennessee Valley Authority
1101 Market St. MS-3S103C
Missionary Ridge Place
Chattanooga, TN 37402
615/751-6708

Andy M. Warren
Resident Service Engineer
Babcock & Wilcox
1990 N. California Blvd., Suite 400
Walnut Creek, CA 94596
415/947-1100

Larry Waterland
Program Manager
Acurex Corporation
485 Clyde Avenue
Mountain View, CA 94039
415/961-5700

Greg Weber
Research Supervisor
Energy & Mineral Research Center
15 North 23rd Street
P.O. Box 8213
Grand Forks, ND 58202-8213
701/777-5222

W. L. Weier
N/A
NV KEMA
P.O. Box 9035
6800 ET Arnhem
THE NETHERLANDS
085/566023

Roy J. Weiskircher
Sr. Env. Control Engineer
USS a Div. of USX Corporation
4000 Tech Center Drive
Monroeville, PA 15146
412/825-2824

Jost O.L. Wendt
Professor
University of Arizona
Dept. of Chemical Engineering
Building 11
Tucson, AZ 85721
602/621-6050

Arthur W. Wesa
Principal Engineer
The Detroit Edison Company
2000 Second Avenue
Detroit, MI 48226
313/237-5117

Phil Westin
Sr. Environmental Engineer
Arco Products Company
1900 W. Crescent Avenue
Anaheim, CA 92803
714/491-6854

Ed Wiken
Chief
Environment Canada
2067 Fairbanks Avenue
Ottawa, Ontario
CANADA
819/997-1090

Dale V. Wilhelm
Environmental Engineer
Tennessee Valley Authority
Environmental Quality Staff
Knoxville, TN 37902
615/632-6695

Ronald Wilkniss
Staff Engineer
Mobil Oil Corporation
3700 W. 190th Street
Torrance, CA 90509
213/212-4587

Steve M. Wilson
Research Engineer
Southern Company Services
P.O. Box 2625
Birmingham, AL 35202
205/877-7835

Phil Winegar
Senior Engineer
New York Power Authority
1633 Broadway
New York, NY 10019
212/468-6729

Johan Witkamp
Engineer
NV KEMA
Utzechtseweg 310
6900 ET Arnhem
THE NETHERLANDS
085/563625

Evan W. Wong
Engineer
Air Resources Board
P.O. Box 2815
Sacramento, CA 95812
916/445-5980

Bernhard J. Wood
Senior Chemist
SRI International
333 Ravenswood Avenue
Menlo Park, CA 94025
415/859-2305

Ralph T. Yang
Professor
State University of New York
Dept. of Chemical Engineering
Buffalo, NY 14260
716/636-2519

Jerry L. Yee
Senior Mechanical Engineer
Hawaiian Electric Company
P.O. Box 2750
Honolulu, HI 96840
808/543-7708

Nancy Yee
Field Engineering
Bay Area Air Quality Mgmnt. Dist.
939 Ellis Street
San Francisco, CA 94109
415/771-6000

Cherif F. Youssef
Research Project manager
Southern California Gas Company
Box 3249 Terminal Annex, M.L. 731D
Los Angeles, CA 90051
818/307-2695

Kenneth P. Zak
Marketing Research & Business Dev.
W. R. Grace & Company
7379 Route 32
Columbia, MD 21044
301/531-4383

Jiansheng Zhao
M. Sc.
University of British Columbia
Chemical Engineering Department
2216 Mail Mall
Vancouver, B.C. V6T 1W5mbia
604/224-8579

Melvin L. Zwillenberg
Principal Staff Engineer, R&D
Public Service Electric & Gas Co.
MC-T16H, 80 Park Plaza
Newark, NJ 07101
201/430-6636